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WATER METALS NUMBER 5. REPORT OF A STUDY CONDUCTED BY ANALYTICAL REFERENCE SERVICE

R. J. Lishka, et al

Environmental Control Administration
Cincinnati, Ohio

1969

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WATER METALS NO. 5

Study Number 34

Report of a Study Conducted by

ANALYTICAL REFERENCE SERVICE

R. J. Lishka and J. H. Parker
TRAINING INSTITUTE

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Consumer Protection and Environmental Health Service
Environmental Control Administration
Cincinnati, Ohio 45202
1969

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FOREWORD

The Analytical Reference Service (ARS) is conducted by the Training Institute of the Environmental Control Administration to evaluate laboratory methods in the environmental field. Cooperative studies by member organizations, who analyze identical samples and critically review methodology, provide the mechanism for:

> Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.
>
> Exchange of information regarding method characteristics.
>
> Improvement or replacement of existing methods by development of more accurate procedures, and development of new methodology for determination of new pollution compounds.

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the membership, consultants, and the ARS staff. Notice of each study is sent to the entire membership. To those who desire to participate, a portion of the study sample is sent, along with data forms for reporting numerical values, a critique of the procedures used, comments on modifications, sources of error, difficulties encountered, or other pertinent factors. The results and comments received are compiled, and a report of each study is prepared.

Initially directed toward examination of water, studies now include methods for analysis of air, milk, and food. Some studies are periodically repeated for the advantage of new members, the evaluation of new methods, or the reeevaluation of existing methods.

The selection of studies is guided by requests from standard methods committees and the responses to questionnaires periodically circulated among the membership, which now includes 294 Federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

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STUDIES COMPLETED AND REPORTED

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium. Studies completed in 1956, 1958, and 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc. Studies completed in 1957 and 1962. These same metals plus silver. Study completed in 1965. Except for the substitution of magnesium for aluminum, these same metals were analyzed by atomic absorption in 1967. Copper, manganese, and aluminum in the presence and absence of interferences. Study completed in 1969.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation by a specified procedure. Studies completed in 1958 and 1961. Fluoride by ion-exchange and fluoride electrode. Study completed in 1969.
Water-Radioactivity	Gross beta activity. Studies completed in 1959 and 1961. Gross beta and strontium-90 activity. Study completed in 1963.
Water-Surfactant	Surfactant in various waters. Studies completed in 1959, 1963, and 1968.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand. Study completed in 1960. Chemical oxygen demand. Study completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium. Study completed in 1962. These same metals plus vanadium. Study completed in 1966.
Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification. Study completed in 1964.
Water-Nutrients	Silicate, phosphate, ammonia nitrogen, organic nitrogen, and nitrate nitrogen. Study completed in 1966.

Water-Phenols	Phenol and 2, 4-dichlorophenol in water by two specified methods. Study completed in 1966.
Water-Cyanides	Potassium cyanide and potassium ferricyanide in water by two specified methods. Study completed in 1967.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass-fiber, high-volume filter mats. Study completed in 1958.
Air-Lead	Filter paper tape impregnated with lead. Study completed in 1960.
Air-Particulates	Microscopic identification of some common atmospheric particulates. Study completed in 1964.
Air-Sulfur Dioxide	Sulfur dioxide in air by a specified method. Study completed in 1963.
Water-Pesticides	Lindane, heptachlor epoxide, DDE, and dieldrin in water. Study completed in 1965. Lindane, heptachlor, aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, endrin, o,p'-DDT, p,p'-DDT, and methoxychlor in water. Study completed in 1968.
Food-Pesticides	DDT in milk. Study completed in 1962. Lindane, heptachlor epoxide, DDE, and dieldrin in milk. Study completed in 1965.

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PREFACE

Aluminum is present in practically all natural waters and may appear additionally in treated waters as a residual from alum coagulation. Perhaps, as a result of the inadequacies of existing methods for determining aluminum (as evidenced by previous ARS studies), there are many conflicting statements in the literature about the amount of aluminum that should be found in filtered water. In any case, there is increasing evidence that very small amounts of aluminum, such as 0.05 mg/l, entering the distribution system can be objectionable. As a result, a recently proposed rapid eriochrome cyanine R (ECR) method for the determination of aluminum in water was tried in our laboratory and appeared in our hands to be at least as accurate as the aluminon method and less time consuming and complicated. Since this procedure was also being considered for inclusion in the 13th edition of Standard Methods for the Examination of Water and Wastewater, this study was devised primarily to evaluate the ECR method and compare it with the existing aluminon standard method for aluminum in the presence and absence of interferences (fluorides, polyphosphates, and other metals).

Inasmuch as one of the samples prepared for this study contained eight other metals (as possible interferences), it seemed appropriate to simultaneously evaluate two new methods for two other metals also proposed for inclusion in the next edition of Standard Methods for the Examination of Water and Wastewater: the formaldoxime colorimetric method for manganese and the disodium bathocuproine disulfonate colorimetric method for copper.

Earl F. McFarren, Chief
Analytical Reference Service

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ACKNOWLEDGMENTS

Michael J. Taras, Chairman, Joint Editorial Board of Standard Methods for the Examination of Water and Wastewater and Kenneth E. Shull, Vice President, Research, Philadelphia Suburban Water Company, the senior author of the ECR procedure, suggested this study to evaluate and compare the ECR procedure with the standard aluminon procedure. Mr. Taras also provided copies of the bathocuproine disulfonate procedure for copper and the formaldoxime procedure for manganese for inclusion in this study.

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PARTICIPANTS IN THIS STUDY

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Calgon Corporation, Pittsburgh, Pennsylvania
California State Department of Public Health, Berkeley
California Water Service Company, San Jose
Ciudad Universitaria, Mexico
Denver Board of Water Commissioners, Colorado
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Dow Chemical Company, Midland, Michigan
Fresno County Department of Public Health, Trenton
Goodyear Atomic Corporation, Piketon, Ohio
Hach Chemical Company, Ames, Iowa
Havens-Emerson, East Patterson, New Jersey
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Illinois State Department of Public Health, Springfield
Illinois State Water Survey, Champaign
Indiana State Board of Health, Indianapolis
Industrial Chemicals, Inc., South Bend, Indiana
Instituto Nacional de Obras Sanitarias, Caracas, Venezuela
Kentucky State Department of Health, Frankfort
Lawrence Experiment Station, Massachusetts
Lincoln-Lancaster City-County Health Department, Lincoln, Nebraska
Los Angeles County Flood Control District, California
Los Angeles Department of Public Works, Playa Del Rey, California
Los Angeles Department of Water and Power, California
Massachusetts Department of Public Health, Amherst
Mekoroth Water Company, Bnei Brak, Israel
Metropolitan Water, Sewage and Drainage Board, Sydney, Australia
Metropolitan St. Louis Sewer District, Missouri
Minneapolis Water Department, Minnesota
Nassau County Department of Health, Hempstead, New York
New York State Department of Health, Albany
North Carolina Department of Water and Air Resources, Raleigh
North Carolina Department of Water Resources, Durham
Ontario Water Resources Commission, Rexdale, Ontario, Canada
Oregon State Board of Health, Portland
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ABSTRACT

In this study, four samples were provided containing between 0.48 and 0.54 mg per liter of aluminum in the presence or absence of fluoride, polyphosphate, and eight other metals including copper and manganese. Participants were provided with copies of the eriochrome cyanine R procedure for aluminum, the bathocuproine disulfonate procedure for copper, and the formaldoxime procedure for manganese, and were requested to preferably analyze the samples by use of these procedures and the aluminon standard methods procedure.

The results indicate that either ECR or aluminon is acceptable in the presence of fluoride if the proper corrective technique is applied.

When polyphosphates are present, both ECR and aluminon give fair results if the fusion technique is used to destroy the phosphate. The less vigorous acid hydrolysis produces similar accuracy and precision with aluminon, but much less precision with ECR. In the presence of other metals, the ECR procedure is significantly more accurate than aluminon but the precision of both methods is poor.

When no interferences are present, both methods show excellent accuracy but unacceptable precision.

The formaldoxime method for manganese gave unacceptable results.

The bathocuproine disulfonate procedure for copper gave excellent results; however, the reagent is expensive.

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WATER METALS NO. 5

DESIGN OF THE STUDY

To evaluate the main interferences in the determination of aluminum, four samples were prepared. In addition to aluminum, sample 1 contained fluoride; sample 2, polyphosphate; sample 3, no interference; and sample 4, eight other metals. To obtain greater stability and to reduce shipping costs, the samples were prepared as concentrated solutions and shipped in sterile, sealed, 25-ml glass ampoules.

The concentrations of aluminum and interferences were such that when the participant diluted, as instructed, 5 ml of each concentrate with enough distilled water to make 1 liter, the samples would contain concentrations likely to be found in water supplies (see Table 1 for composition of samples).

Table 1. COMPOSITION OF SAMPLES

	mg/l in diluted sample			
	Sample 1	Sample 2	Sample 3	Sample 4
Aluminum (Al)	0.48	0.54	0.52	0.50
Fluoride (F)	0.75			
Polyphosphate (PO_4)		2.5		
Copper (Cu)				1.00
Iron (Fe)				0.30
Manganese (Mn)				0.05
Zinc (Zn)				0.65
Silver (Ag)				0.15
Cadmium (Cd)				0.05
Chromium (Cr)				0.11
Lead (Pb)				0.07

In analyzing the samples, the participants were requested to preferably use the aluminon standard method and the procedures for which instructions were sent with the sample: the eriochrome cyanine R method for aluminum, the bathocuproine disulfonate method for copper, and the formaldoxime method for manganese (see Appendices D, E and F).

TREATMENT OF THE DATA

As the results of analysis were received from each participant, the data were reviewed, and, in the case of a suspected mathematical error, the reporting laboratory was asked to check the calculations and to submit

a corrected value if an error was found. Those participants who failed to furnish an identification of the specific procedure used also were contacted for this information

The data were then coded and analyzed by computer for normality of distribution and subsequent rejection of outliers that were nonrepresentative because of errors in calculation, dilution, or other indeterminate factors.

The results for each method were also plotted on normal probability paper as a visual check on normality of distribution and the possible presence of outliers. After rejection of outliers, the data were then statistically analyzed by computer for precision and accuracy (see Appendices G and I).

Bar graphs are included in the text to provide a pictorial display of the data. Rejected values are indicated by broken bars, and values are given for bars off the scale of the chart. Although some bar graphs display results for more than one method, outliers were determined only for the individual methods rather than for the overall results.

Since the prime objective of the study was to evaluate the ECR method for aluminum and compare it with the standard aluminon procedure, the results obtained by these methods were evaluated according to the various modifications used to eliminate interferences, and the separate techniques were statistically compared.

Results were also submitted by five participants who each used a different method other than the two being studied. Unfortunately, a single result for a specific procedure does not permit statistical evaluation; but these results are so generally excellent that they have been shown in the statistical summary tables and may warrant further investigation.

The results for manganese are similarly evaluated. The formaldoxime method was used with six different techniques for eliminating interferences.

The analysis for copper was performed by use of six distinctly different methods with no separate modifications.

The individual results tabulated for aluminum, copper, and manganese in appendices A, B and C, respectively, are catalogued there according to the method or modification number listed under aluminum, copper or manganese in the bibliography of this report.

RESULTS

Sample 1. Aluminum with fluoride interference (Table 2; Figures 1, 2, 3 and 4)

ECR method without any corrective treatment gave good accuracy and precision, according to four results, which are, however, too few to draw reliable conclusions. One participant hydrolyzed the sample to eliminate possible phosphate interference and also obtained a good result. Poor results were obtained when both the phosphate hydrolysis and fluoride correction were used on the same sample. The least precise technique seemed to be the use of fusion to eliminate fluorides. Good accuracy but only fair precision was obtained when fluoride was added to the standards or when the provided correction curves were used, and there was no significant difference between the two techniques.

The aluminon procedure in general produced poor results, except for the technique of adding fluoride to the standards, which produced good accuracy and fair precision, nearly the same as for the ECR procedure. The mean of the ECR values was high, however, while the mean of the aluminon values was low.

Both methods appear equally acceptable in the presence of fluoride interference if a corrective technique is applied. If no correction for fluoride is used in the aluminon procedure, the results tend to be low and erratic.

The overall ECR results, regardless of corrective technique, produced excellent accuracy and poor precision. The overall aluminon results showed much less accuracy, which is not statistically significant, however, because of the poor precision.

Table 2. SUMMARY OF DATA ON SAMPLE 1 (0.48 mg per liter of aluminum with fluoride interference)

Method	Number of Results	Number of Outliers	Mean	Mean Error	Standard Deviation	Relative Error	Relative Std. Dev.	95% Tol. Limits
Eriochrome Cyanine R								
No correction	4	1	0.495	+0.015	0.034	3.1	6.9	0.218
Hydrolysis	1	-	0.470	-------	------	----	----	------
Hydrolysis and F^- correction	7	0	0.540	+0.060	0.368	12.4	68.2	1.474
Fusion or distillation	4	0	0.390	-0.090	0.289	18.8	74.2	1.843
F^- added to standards	17	0	0.514	+0.034	0.116	7.1	22.5	0.330
Curve correction for F^-	16	1	0.469	-0.011	0.120	2.3	25.5	0.347
Aluminon								
No correction	11	2	0.324	-0.155	0.180	32.4	55.6	0.588
Hydrolysis	4	0	0.552	+0.072	0.232	14.9	42.0	1.475
Hydrolysis and F^- correction	1	-	0.300	-------	------	------	----	------
Fusion or distillation	11	1	0.456	-0.025	0.214	5.1	47.0	0.698
F^- added to standards	7	0	0.444	-0.036	0.097	7.6	21.8	0.388
9th & 10th ed. method	2	0	0.575	-------	------	----	----	------
Modified	1	-	0.500	-------	------	----	----	------
Chrome Azurol S	1	-	0.500	-------	------	----	----	------
Fluorometric	1	-	0.470	-------	------	----	----	------
Ferron-orthophenanthroline	1	-	0.470	-------	------	----	----	------
Atomic Absorption	1	-	0.570	-------	------	----	----	------
ECR overall	51	0	0.489	+0.009	0.200	1.9	40.8	0.474
Aluminon, overall	34	3	0.417	-0.063	0.191	13.0	45.7	0.478

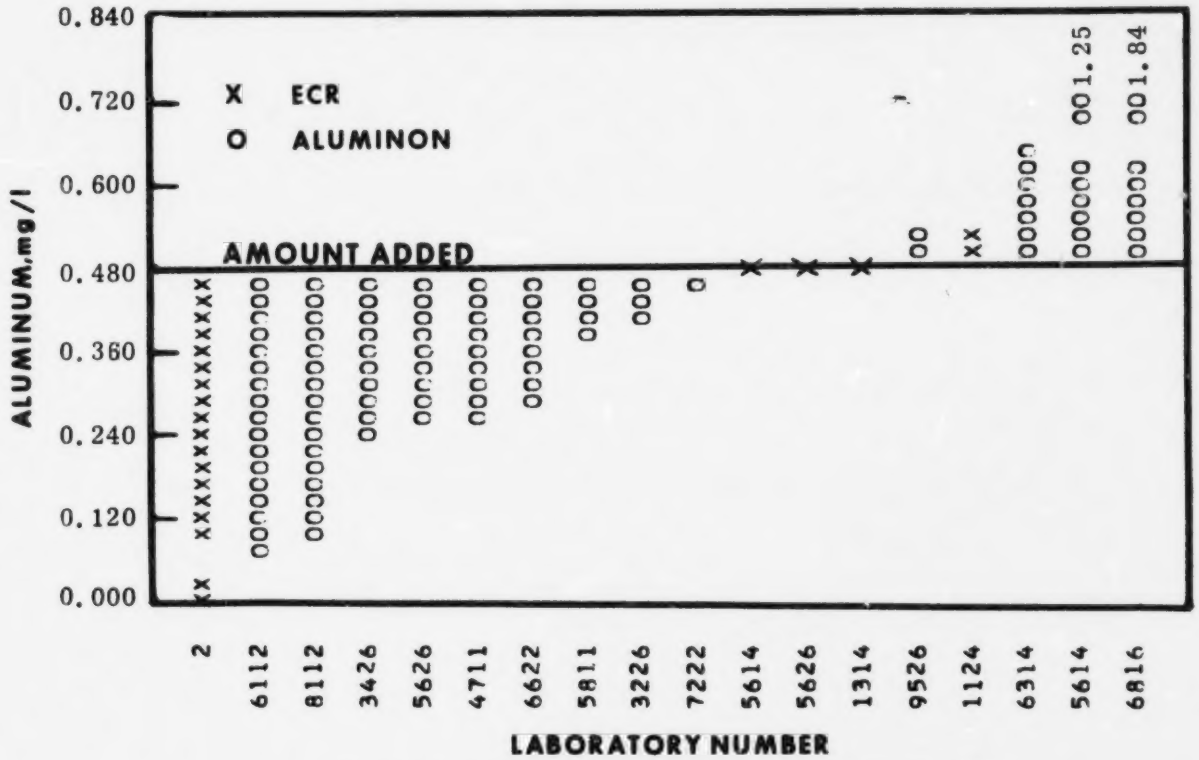

Figure 1. Bar graph for aluminum in sample 1 with no correction.

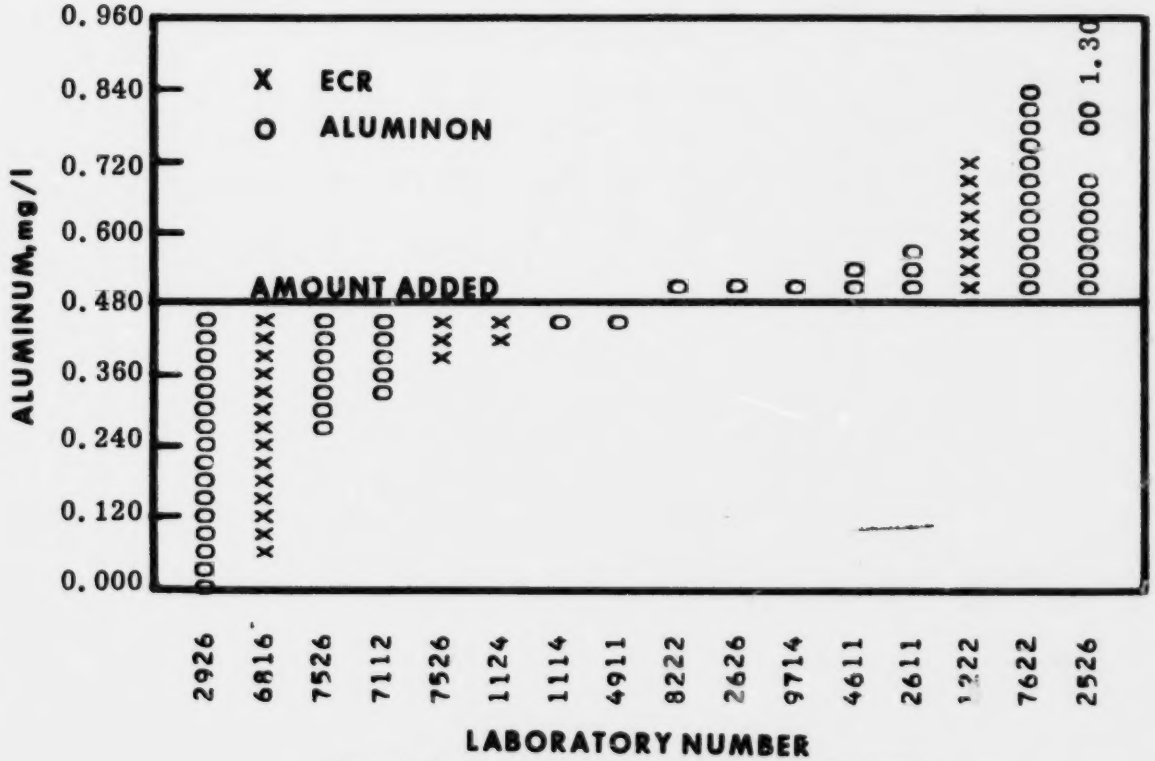

Figure 2. Bar graph for aluminum in sample 1 with fusion.

Figure 3. Bar graph for aluminum in sample 1 with fluoride added to standards.

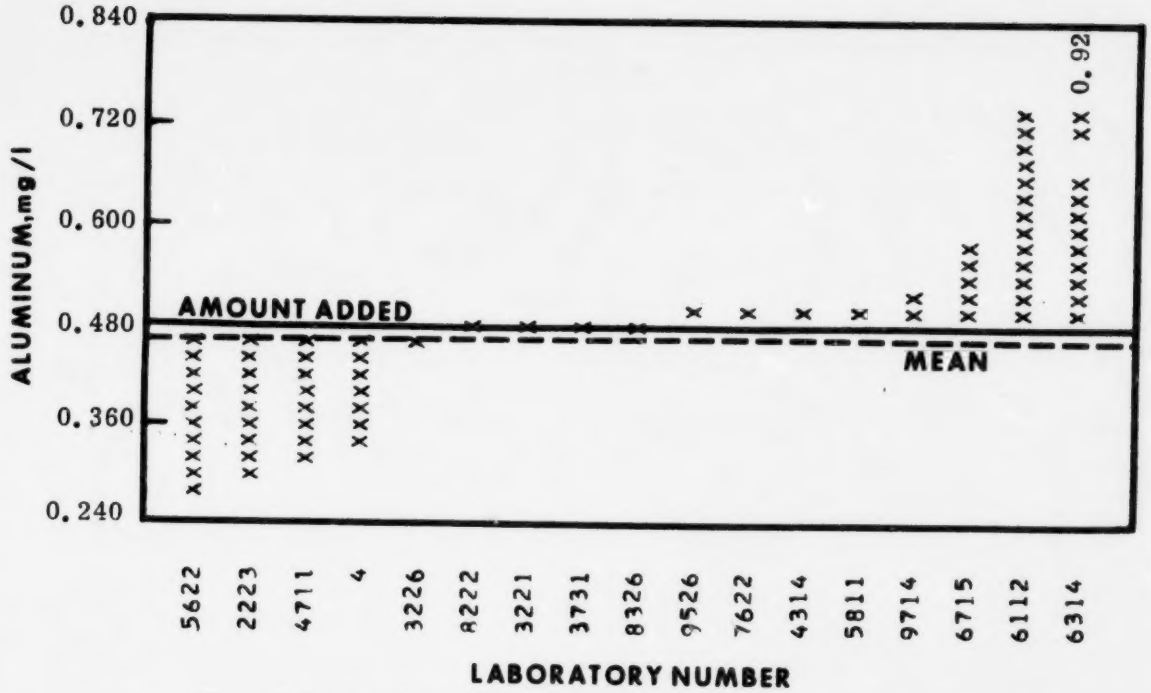

Figure 4. Bar graph for aluminum in sample 1 by ECR using curves for correction.

Sample 2. Aluminum with polyphosphate interference (Table 3; Figures 5, 6, and 7)

Both the ECR and aluminon procedures produced good accuracy but poor precision when no corrective technique was applied to eliminate phosphate interference. Acid hydrolysis produced excellent accuracy but poor precision with ECR. With aluminon, however, the precision was much better, and the accuracy was good although less than with ECR. When both the hydrolysis and a fluoride correction were applied, the results were poor for both ECR and aluminon. The fusion technique, designed to eliminate both fluoride and phosphate interference, produced fair results with both ECR and aluminon but was used by too few participants to warrant a conclusion. Surprisingly, the participants who erroneously applied a fluoride correction to the ECR procedure, either by use of the curves or by adding fluoride to the standards, obtained fair results. Obviously, any correction added to the results obtained will partially compensate for the low results caused by the action of polyphosphate.

It is evident that the presence of polyphosphate tends to produce low results by both methods. The destruction of polyphosphate by either hydrolsis or fusion will produce acceptable results with aluminon. With ECR, the precision is unacceptable when hydrolysis is used, but the fusion technique may be satisfactory.

The overall results for both ECR and aluminon, regardless of corrective technique, show acceptable accuracy but poor precision.

Table 3. SUMMARY OF DATA ON SAMPLE 2 (0.54 mg per liter of aluminum with polyphosphate interference)

Method	Number of Results	Number of Outliers	Mean	Mean Error	Standard Deviation	Relative Error	Relative Std. Dev.	95% Tol. Limits
Eriochrome Cyanine R								
No correction	12	0	0.492	-0.048	0.242	8.7	49.2	0.768
Hydrolysis	16	0	0.533	-0.007	0.236	1.3	44.3	0.686
Hydrolysis and F^- correction	6	1	0.269	-0.271	0.143	50.1	52.9	0.629
Fusion or distillation	3	1	0.461	-0.079	0.034	14.7	7.4	0.338
F^- added to standards	4	1	0.450	-0.090	0.125	16.6	27.8	0.796
Curve correction for F^-	5	0	0.447	-0.093	0.146	17.2	32.7	0.742
Aluminon								
No correction	16	1	0.491	-0.049	0.237	9.0	48.2	0.688
Hydrolysis	8	2	0.484	-0.056	0.079	10.3	16.4	0.296
Hydrolysis and F^- correction	1	-	0.330	------	-----	----	----	-----
Fusion or distillation	6	1	0.461	-0.079	0.078	14.7	17.0	0.347
F^- added to standards	1	-	0.375	------	-----	----	----	-----
9th & 10th ed. method	2	0	0.600	------	-----	----	----	-----
Modified	1	-	0.400	------	-----	----	----	-----
Chrome Azurol S	1	-	0.580	------	-----	----	----	-----
Fluorometric	1	-	0.500	------	-----	----	----	-----
Ferron-orthophenanthroline	1	-	0.500	------	-----	----	----	-----
Atomic Absorption	1	-	0.540	------	-----	----	----	-----
ECR overall	48	1	0.469	-0.071	0.234	13.2	49.8	0.559
Aluminon, overall	35	1	0.491	-0.049	0.213	9.0	43.3	0.530

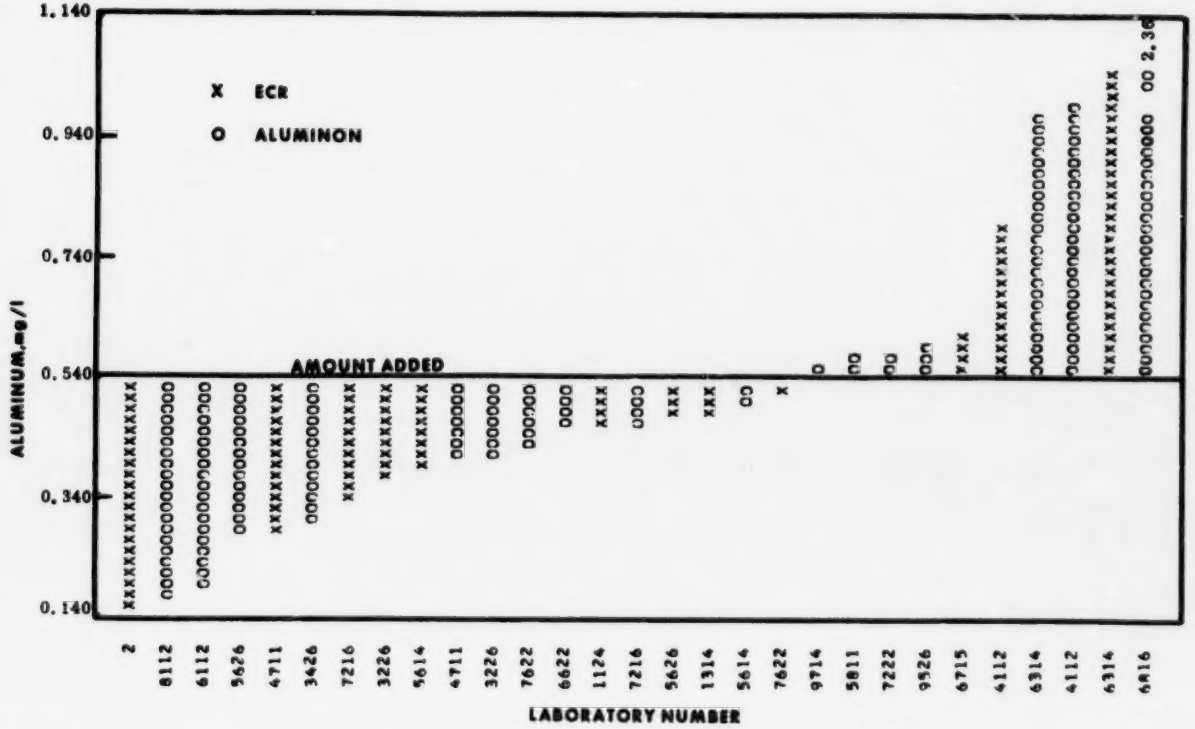

Figure 5. Bar graph for aluminum in sample 2 with no correction.

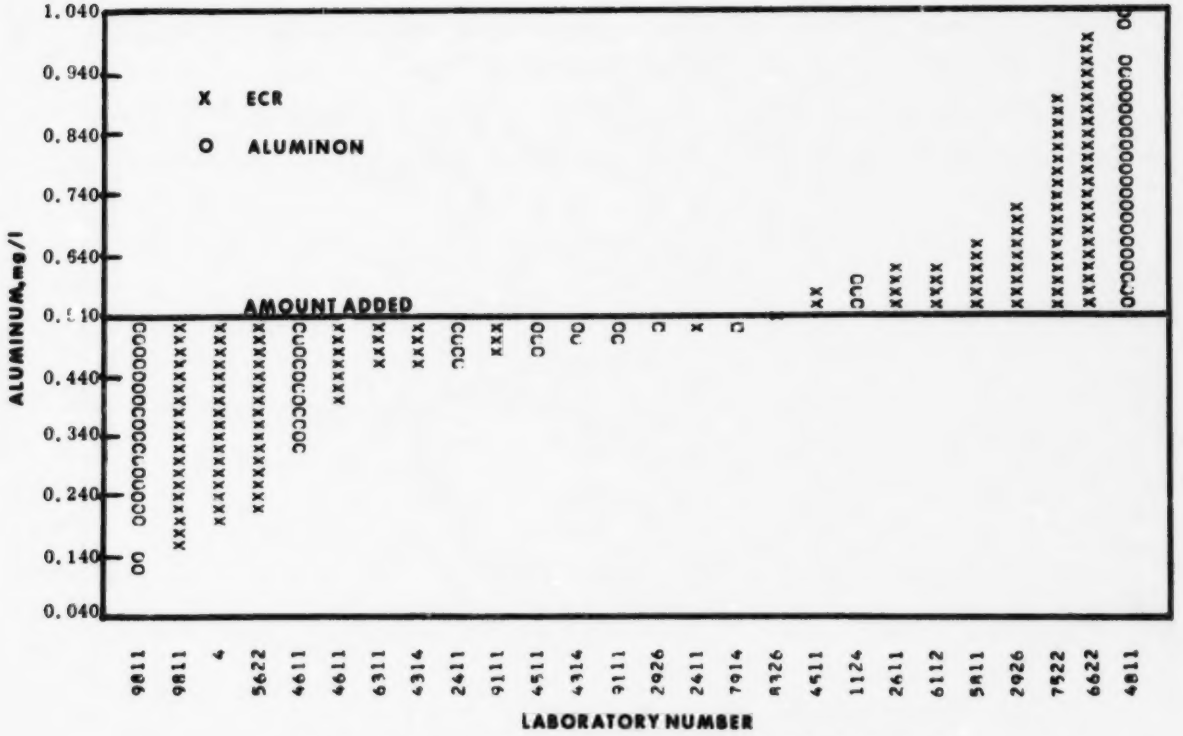

Figure 6. Bar graph for aluminum in sample 2 by hydrolysis.

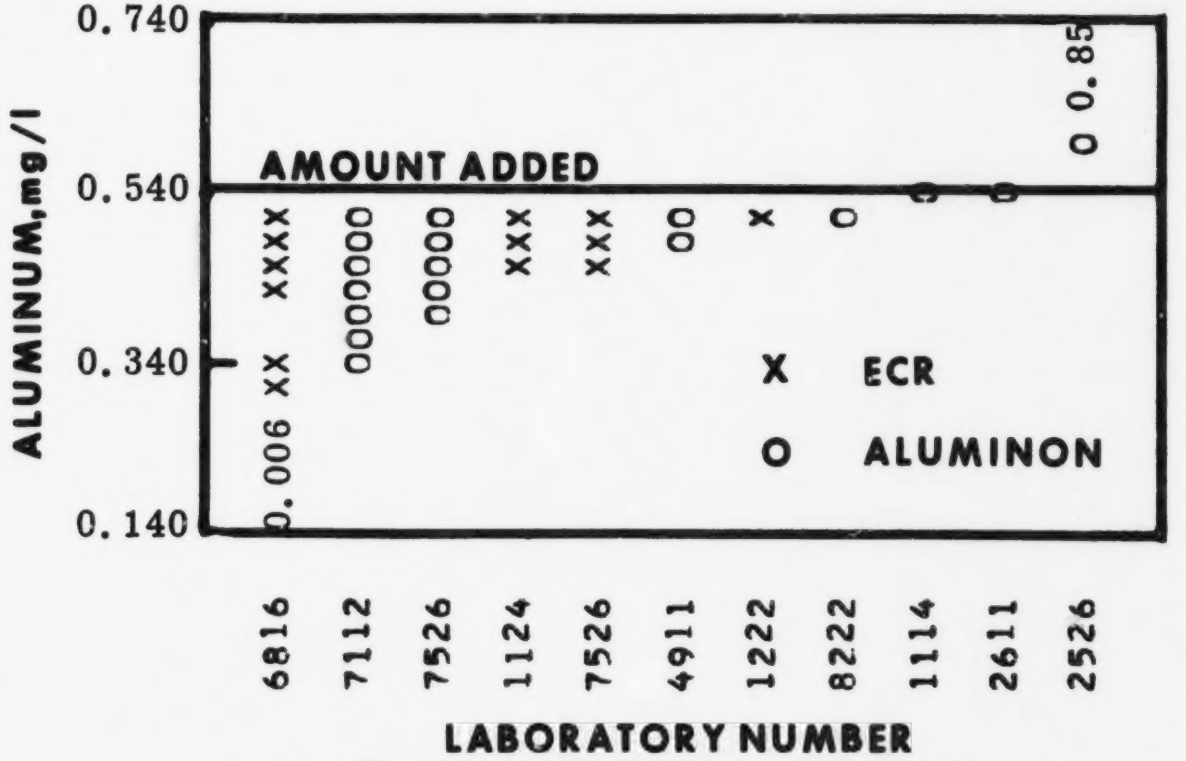

Figure 7. Bar graph for aluminum in sample 2 with fusion.

Sample 3. Aluminum with no interference (Table 4; Figures 8 and 9)

In the absence of interference, both the ECR and aluminon procedures produced good accuracy but poor precision when no correction was applied When either hydrolysis or fusion was performed by either method, in general, both accuracy and precision were poor, but there is insufficient data to draw any firm conclusions. As might be expected, the application of an unwarranted fluoride correction also produced poor results.

Both methods produce excellent accuracy and poor precision in the absence of interference, but the simplicity and speed of the ECR procedure would seem to make it preferable to the aluminon procedure.

Table 4. SUMMARY OF DATA ON SAMPLE 3 (0.52 mg per liter of aluminum with no interference)

Method	Number of Results	Number of Outliers	Mean	Mean Error	Standard Deviation	Relative Error	Relative Std. Dev.	95% Tol. Limits
Eriochrome Cyanine R								
No correction	27	1	0.511	-0.009	0.176	1.7	34.4	0.456
Hydrolysis	3	0	0.681	+0.161	0.374	31.0	54.8	3.704
Hydrolysis and F^- correction	5	0	0.338	-0.182	0.257	35.1	76.1	1.305
Fusion or distillation	4	0	0.465	-0.055	0.381	10.6	82.0	2.428
F^- added to standards	5	0	0.671	+0.151	0.175	29.0	26.1	0.889
Curve correction for F^-	4	0	0.595	+0.075	0.124	14.4	20.8	0.788
Aluminon								
No correction	23	2	0.491	-0.029	0.170	5.6	34.6	0.454
Hydrolysis	3	0	0.600	+0.080	0.348	15.4	58.0	3.448
Hydrolysis and F^- correction	1	-	0.420	------	-----	----	----	-----
Fusion or distillation	6	0	0.408	-0.112	0.123	21.5	30.1	0.543
F^- added to standards	1	-	0.400	------	-----	----	----	-----
9th & 10th ed. method	2	0	0.700	------	-----	----	----	-----
Modified	1	-	0.510	------	-----	----	----	-----
Chrome Azurol S	1	-	0.520	------	-----	----	----	-----
Fluorometric	1	-	0.490	------	-----	----	----	-----
Ferron-orthophenanthroline	1	-	0.490	------	-----	----	----	-----
Atomic Absorption	1	-	0.540	------	-----	----	----	-----
ECR, overall	48	1	0.523	+0.003	0.223	0.6	42.7	0.534
Altminon, overall	34	2	0.481	-0.039	0.177	7.4	36.9	0.444

Figure 8. Bar graph for aluminum in sample 3 by ECR with no correction.

Figure 9. Bar graph for aluminum in sample 3 by aluminon with no correction

Sample 4. Aluminum with other metal interference (Table 5; Figures 10 and 11)

In the presence of other metals, and with no correction, the ECR procedure was significantly more accurate than the aluminon procedure. The precision, however, was somewhat less with ECR. Both methods tended to produce slightly high results. When the samples were hydrolyzed, the results were poor by both methods. The fusion technique produced better accuracy, but the precision is even poorer and, as before, unacceptable. Erroneously adding a fluoride correction to already high results also contributed to the inaccuracy.

The older aluminon procedure, appearing last in the 10th edition of Standard Methods for the Examination of Water and Wastewater, was used by two participants and appears to be much more subject to interference by other metals.

Again, the ECR procedure appears to be the preferred method because of its simplicity and better accuracy. The precision, however, is unsatisfactory.

Table 5. SUMMARY OF DATA ON ALUMINUM IN SAMPLE 4
(0.50 mg per liter of aluminum and eight other metals as interference)

Method	Number of Results	Number of Outliers	Mean	Mean Error	Standard Deviation	Relative Error	Relative Std. Dev.	95% Tol. Limits
Eriochrome Cyanine R								
No correction	26	2	0.531	+0.031	0.153	6.2	28.8	0.400
Hydrolysis	2	0	0.550	------	-----	----	----	-----
Hydrolysis and F^- correction	5	1	0.297	-0.203	0.157	40.6	53.0	0.799
Fusion or distillation	4	0	0.390	-0.110	0.281	22.0	72.1	1.793
F^- added to standards	5	0	0.681	+0.181	0.181	36.2	26.5	0.918
Curve correction for F^-	4	0	0.578	+0.078	0.098	15.5	17.0	0.625
Aluminon								
No correction	22	3	0.566	+0.066	0.120	13.1	21.1	0.322
Hydrolysis	3	0	0.803	+0.303	0.170	60.7	21.2	1.690
Hydrolysis and F^- correction	1	-	0.520	------	-----	----	----	-----
Fusion or distillation	6	0	0.597	+0.097	0.164	19.4	27.4	0.723
F^- added to standards	1	-	0.542	------	-----	----	----	-----
9th & 10th ed. method	2	0	1.370	------	-----	----	----	-----
Modified	1	-	0.710	------	-----	----	----	-----
Chrome Azurol S	1	-	0.530	------	-----	----	----	-----
Fluorometric	1	-	0.520	------	-----	----	----	-----
Ferron-orthophenanthroline	1	-	0.520	------	-----	----	----	-----
Atomic Absorption	1	-	0.600	------	-----	----	----	-----
ECR, overall	48	1	0.538	+0.038	0.215	7.6	40.0	0.515
Aluminon, overall	34	2	0.605	+0.105	0.163	21.0	27.0	0.409

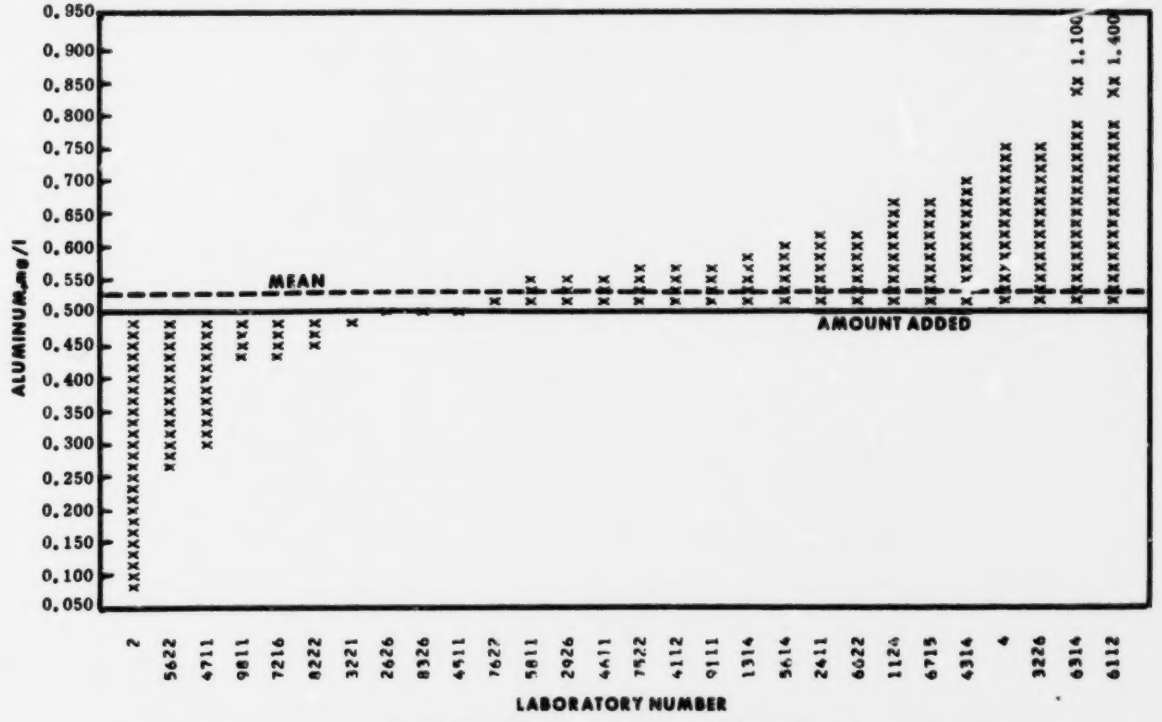

Figure 10. Bar graph for aluminum in sample 4 by ECR with no correction.

Figure 11. Bar graph for aluminum in sample 4 by aluminon with no correction.

Copper in Sample 4 (Table 6; Figures 12, 13, and 14)

The majority of participants used the bathocuproine disulfonate procedure, as requested, and obtained excellent results. Half as many used cuprethol with equally good results. Atomic absorption also shows excellent precision and accuracy, with a relative error of only slightly more than 1 percent. Considering the overall results obtained by use of six different procedures, the accuracy and precision as shown by the relative error of 0.13 percent and relative standard deviation of 3.53 percent are excellent. Any of the methods used are suitable for measuring copper at this concentration. The bathocuproine reagents, however, are very expensive.

Table 6. SUMMARY OF DATA ON COPPER IN SAMPLE 4
(1.00 mg per liter of copper)

Method	Number of Results	Number of Outliers	Mean	Mean Error	Standard Deviation	Relative Error	Relative Std. Dev.	95% Tol. Limits
Bathocuproine Disulfonate	33	3	1.003	+0.003	0.042	0.3	4.1	0.104
Cuprethol Standard Method A	17	1	0.990	+0.010	0.027	1.0	2.7	0.077
Bathocuproine Standard Method B	1	-	1.140	------	-----	---	---	-----
Atomic Absorption	10	2	1.013	+0.013	0.021	1.3	2.0	0.070
Carbamate, 9th ed. Standard Method	1	-	1.020	------	-----	---	---	-----
Zincon	1	-	0.850	------	-----	---	---	-----
Overall	61	8	1.001	+0.001	0.035	0.1	3.5	0.082

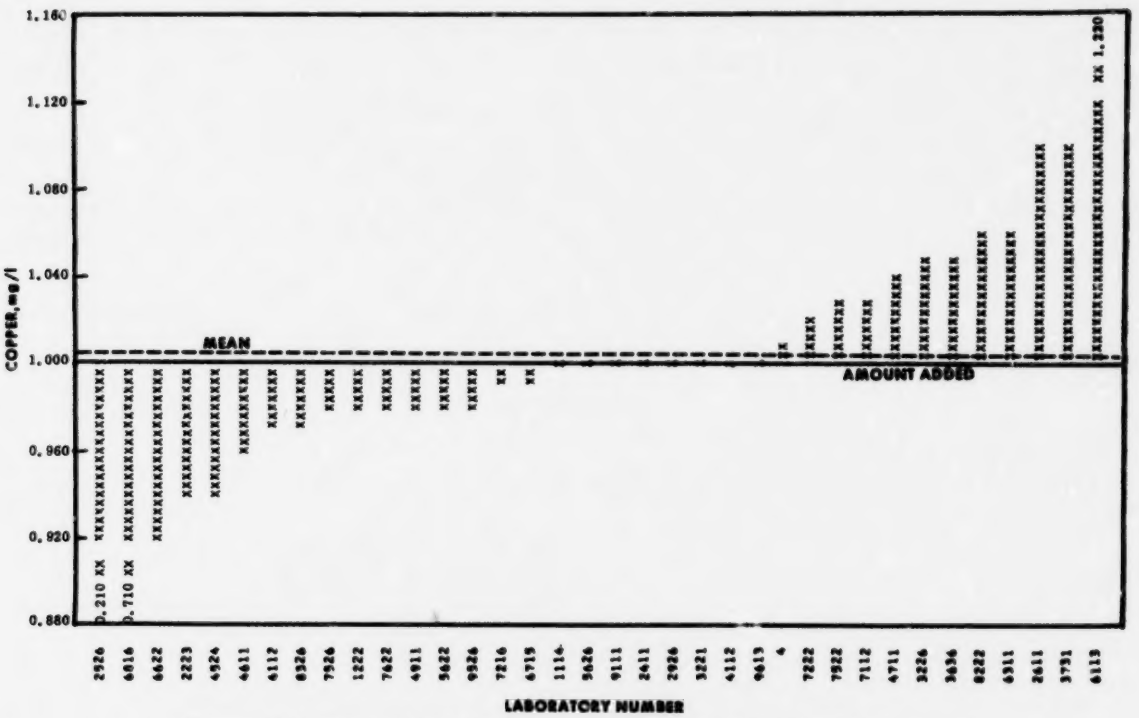

Figure 12. Bar graph for copper in sample 4 by bathocuproine disulfonate.

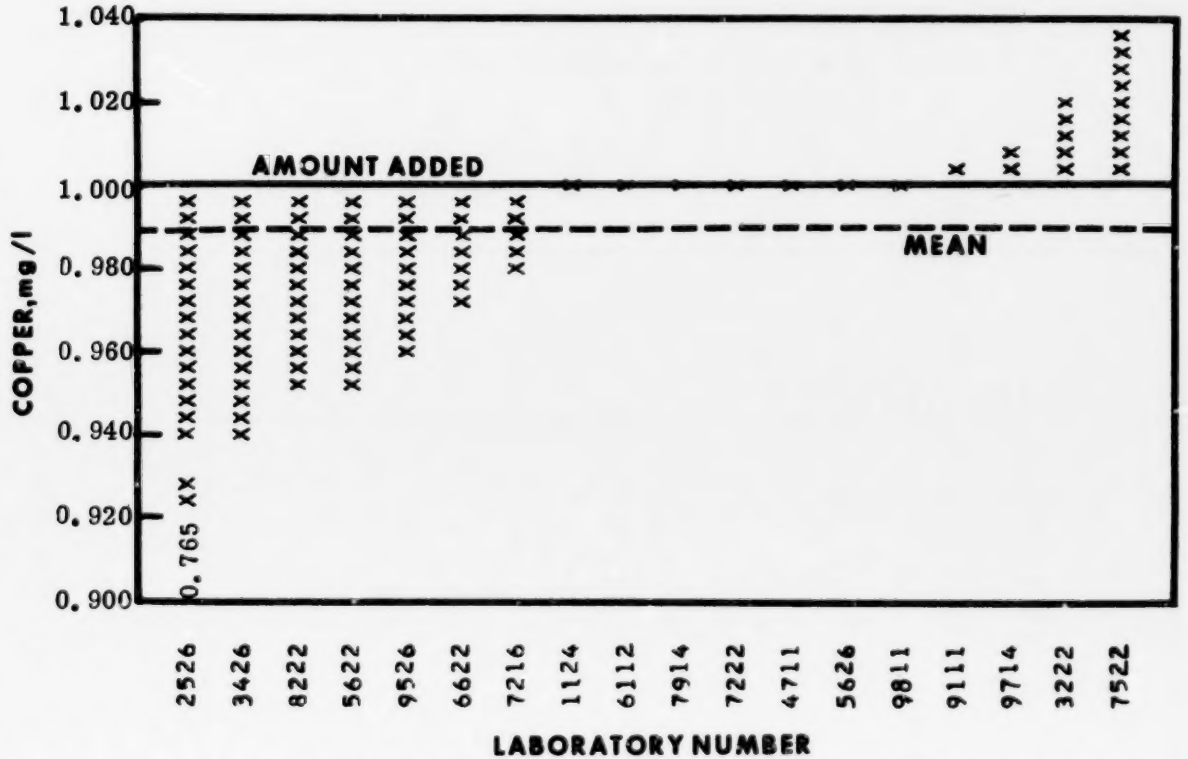

Figure 13. Bar graph for copper in sample 4 by cuprethol.

Figure 14. Bar graph for copper in sample 4 by atomic absorption.

Manganese in Sample 4 (Table 7; Figures 15, 16, and 17)

Thirty-five results for the measurement of manganese were obtained by some modification of the formaldoxime method. Regardless of the procedure used to eliminate interference, the accuracy and precision of this method were unacceptable. Since the results were predominantly high, it appears likely that a positive interference, probably due to iron, was present in spite of the corrective techniques used.

The persulfate, periodate, and atomic absorption procedures produced excellent accuracy, but only the periodate results show acceptable precision. Unfortunately, a total of only four results by this method does not warrant a firm conclusion. In fact, a previous study based on fourteen results shows the method to be unacceptable.

Atomic absorption would be the method of choice, if available, because of its simplicity, speed of analysis, and greater precision than the persulfate method.

Table 7. SUMMARY OF DATA ON MANGANESE IN SAMPLE 4
(0.05 mg per liter of Manganese)

Method	Number of Results	Number of Outliers	Mean	Mean Error	Standard Deviation	Relative Error	Relative Std. Dev.	95% Tol. Limits
Formaldoxime								
No correction	9	2	0.079	+0.029	0.041	58.0	51.4	0.143
Cyanide added	11	2	0.074	+0.027	0.033	53.4	43.4	0.108
Iron added to standards	11	2	0.081	+0.031	0.062	2	76.3	0.200
Standard addition	1	-	0.100	------	-----	----	----	-----
Heating	1	-	0.010	------	-----	----	----	-----
Iron and cyanide added	2	0	0.244	------	-----	----	----	-----
Overall	41	0	0.114	+0.064	0.088	127.5	77.1	0.214
Persulfate	17	2	0.054	+0.004	0.027	7.2	50.3	0.077
Periodate	4	1	0.051	+0.001	0.003	1.5	5.9	0.020
Atomic absorption	13	0	0.048	+0.002	0.011	4.5	23.1	0.034

Figure 15. Bar graph for manganese in sample 4 by formaldoxime.

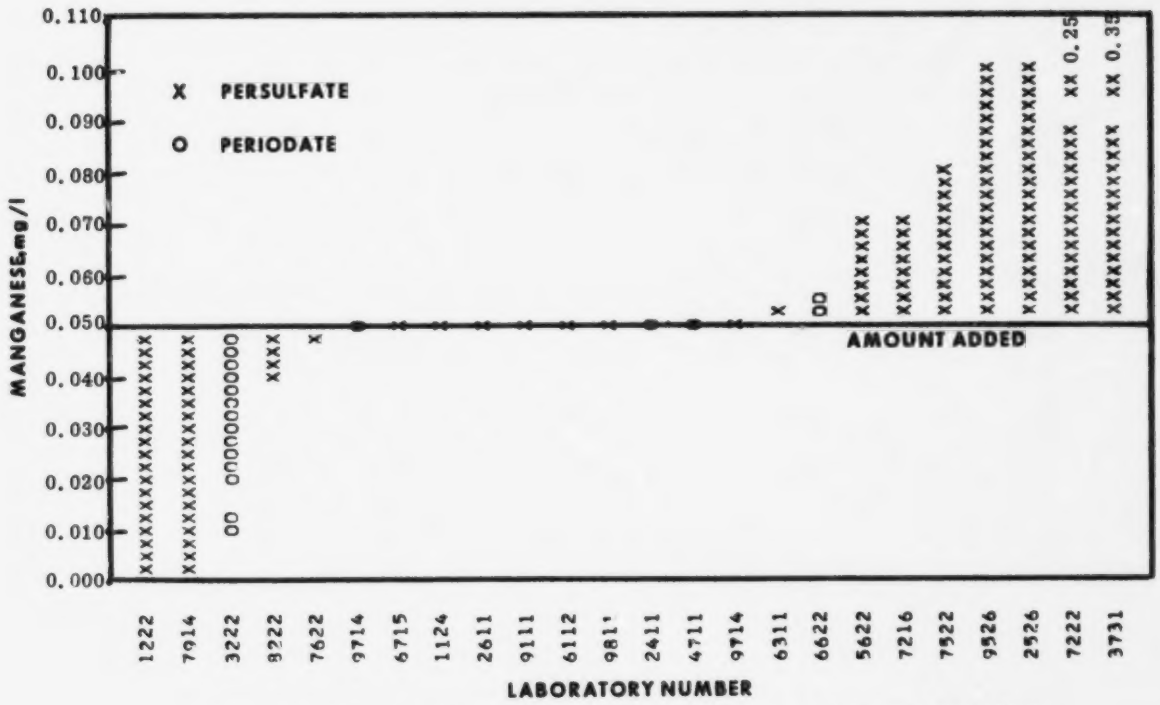

Figure 16. Bar graph for manganese in sample 4 by persulfate and periodate.

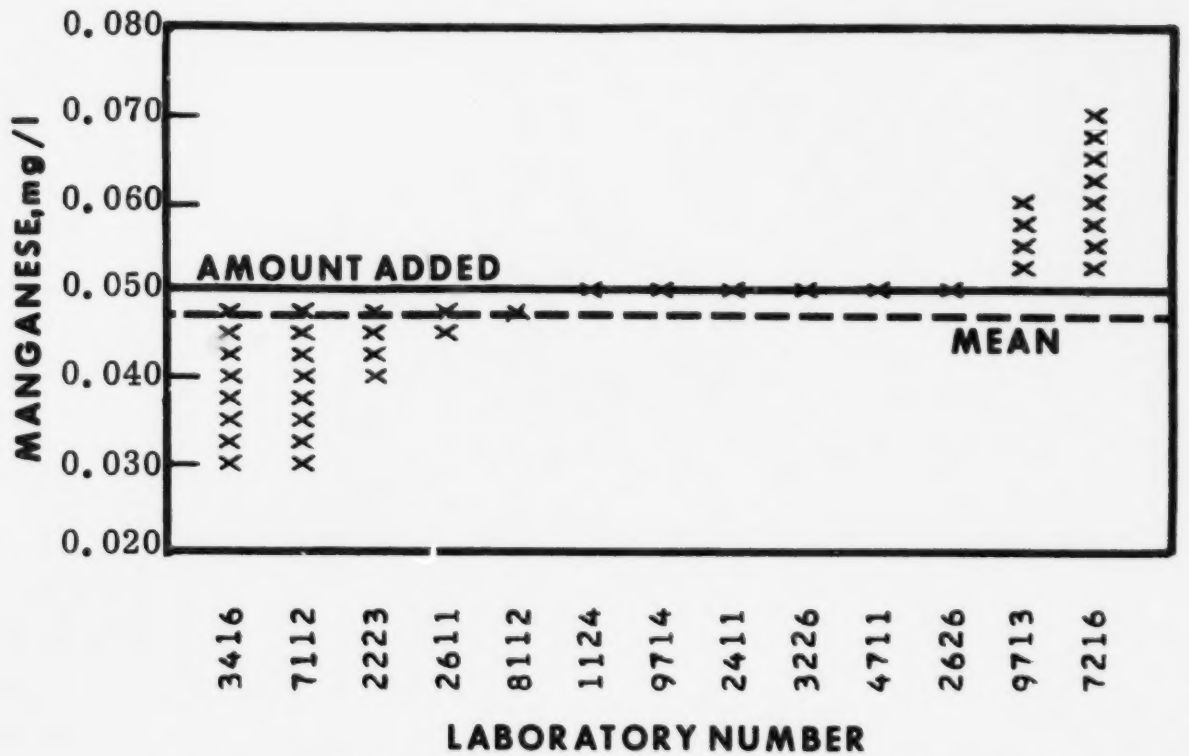

Figure 17. Bar graph for manganese in sample 4 by atomic absorption.

DISCUSSION

In this study, the participants were requested to use either the provided ECR procedure, the aluminon standard method, or both, for the analysis of aluminum. It was left up to the analyst to select and report the techniques used to eliminate interference by fluoride and polyphosphate. Unfortunately, many participants failed to analyze for polyphosphate and reported no interference because the orthophosphate concentration was below the stated interference level of 10 mg/l. Many incorrect values were reported for the fluoride content of sample 1, and several analysts reported finding fluoride in the other three samples, which were free of fluoride, and improperly applied a correction.

One participant, among several who did not understand that the purpose of the study was to evaluate specified procedures, used his own fluoride correction curves and, in addition, stated that he added fluoride to the standards. These results, being valueless, were omitted.

Some participants reported using ECR type dyes from suppliers other than those listed in the procedure. The characteristics and required concentration of these dyes may not have been investigated and may have caused some difficulty.

Some participants expressed concern that the specified standards containing 0-0.28 mg/l Al were not high enough to include the concentrations of aluminum in the samples. The explanation can be found in the statement in paragraph 1.1 of the ECR procedure: "The optimum aluminum range lies between 0.02 and 0.35 mg/l, but can be extended upward by sample dilution."

Two typographical errors have been found in the procedures provided. In the ECR procedure, it is stated that "Sulfates do not interfere up to a concentration of 2000 mg/l." The correct concentration should read 200 mg/l. In the formaldoxime method for manganese, the instructions for the preparation of a standard curve specify a "range of 0 to 3.0 mg/l (0 to 30 mg Mn)--." Obviously, it should read "(0 to 30 μg Mn)" since a 10 ml volume is specified.

COMMENTS OF THE PARTICIPANTS

Aluminum - Eriochrome Cyanine R Procedure

1. The ECR method is very time consuming when interferences must be removed or corrected for.

2. When fluoride was added to the standards, the resulting curve was very erratic. This appears to be a satisfactory procedure without interfering fluoride, but a poor one with fluoride present.

3. We noted that the absorbancies of the standards when treated for phosphate interference were considerably higher than the standards not treated. Also, we found that it was difficult to heat the samples to just below boiling. When fluorides were added to the standards, no differences in the absorbances were found.

4. Color fading of the aluminum - ECR complex was noticed after about 8 minutes, when the maximum color was developed.

5. This method proved inconsistent, especially in reproducing the standard curve.

6. Variance in room temperature had a great effect on the color development. Many factors affect the color reaction of eriochrome cyanine R and require meticulous control.

7. We found that our standard curve for aluminum did not follow Beer's Law, even at low concentrations, although it was reproducible. We also had some difficulty correcting for aluminum in our reagents, which was 0.008 ± 0.002 mg/l.

8. Our graph for fluoride correction differed markedly from the graph supplied along with the method. We found that fluoride gave an increase in absorbance while the supplied graph shows a decrease in absorbance with fluoride concentration.

9. Results not very reproducible.

10. Color changed continuously. Absorbance increased approximately 6 to 8 units per minute.

11. Although calibration curve was very reproducible, results on samples 1, 2, and 4 were not.

12. The acid digestion for phosphate removal was long and subsequent neutralization tedious.

Aluminum - Aluminon Procedure

1. Method is very involved for routine analysis.

2. Results by this method are reported only to the nearest tenth because of high reagent blank.

3. Removal of fluoride by the acid-fusion treatment was difficult and a questionable procedure.

4. Extra care had to be exercised to insure constant boiling.

Copper - Bathocuproine Disulfonate Procedure

1. A very good method, both rapid and reproducible.

2. Reagent is too expensive at $22.50 per gram.

3. There appears to be no advantage in either the time saved or in the simplicity of technique of this method over the cuprethol method, which is more sensitive and costs less (44¢ per gram vs. $22.50 per gram).

4. This is easier and just as accurate as the cuprethol method.

5. The slope of the calibration curve was very poor, although checks on it showed very good reproducibility.

Manganese - Formaldoxime Procedure

1. Color development in standards was immediate, but in the unknown the color did not develop until midway in the heating period.

2. Used sodium cyanide for iron interference. Method seems quite satisfactory but would prefer to run it under a hood.

3. In previous work with the formaldoxime method, we were unable to reproduce our results satisfactorily.

4. Color development is poor. Correction for presence of iron is time consuming for routine analysis of many samples.

5. Manganese was undetectable in original dilution of unknown. Determination was made on sample concentrated by a factor of 8.

6. Difficult to compensate for iron interference. Cyanide was used but would not recommend it.

7. Determined iron by o-phenanthroline method and added iron to standards. Color continued to develop well after the 20-minute wait interval and negated chance for stable percent transmission readings.

8. This method was very unsatisfactory. Iron and phosphate were compensated for as suggested (the amount of lead in acetic acid was not clear). The standard curve was linear and reproducible, but the sample ranged from a negative to above the highest standard. The results were not even slightly reproducible.

9. Compensated for phosphate by adding lead in acetic acid. This was unsatisfactory because the amounts of reagents to be added were not known.

10. This sample was off color at the end of 20 minutes, as compared to prepared standards.

11. Heating at 65°C caused a dark color, blank darker than 1 mg/l of standard. Bad peptone? Attempt to remove phosphate failed, and sample became turbid with white precipitate when sodium cyanide was added. Need more details. Less trouble to concentrate sample for persulfate method.

12. Procedure did not give good results. Cyanide used to remove iron interference caused yellow discoloration.

13. Could not develop a stable standard curve as control samples produced erratic results.

14. Standards did not conform to Beer's Law. Results inconclusive.

15. This method does not appear as sensitive as stated. It was necessary to concentrate 200 ml to 50 ml to get a value.

16. Procedure not clear whether cyanide is to be used even though iron is added to the standards.

17. Results for manganese were corrected by adding iron to standards, which gave a value of 0.09 mg/l manganese. The sodium cyanide sequestering gave a value of over 0.2 mg/l.

Manganese - Persulfate Procedure

1. An aliquot of 250 ml was concentrated to 100 ml in order to make the determination.

2. Color fades rapidly.

3. Because of the lack of sensitivity of this method, concentration of sample was required to obtain a result.

4. Sample concentrated in order to develop enough color.

SUMMARY AND CONCLUSIONS

The ECR and aluminon procedures both depend on the same type of reaction: the formation of a reddish lake by reacting aluminum with

an organic dye. Both are similarly affected by the presence of fluoride or polyphosphate and require special treatment to remove these interferences.

The correction for fluoride by adding fluoride to the standards was equally successful for the ECR procedure or for the aluminon. The use of the provided correction curves for ECR also gave good results.

The acid hydrolysis of polyphosphate used with ECR rather than with aluminon produced better accuracy but less precision. There is a tendency toward high results in both methods when this technique is applied to samples not containing polyphosphates.

In the presence of other metals, the ECR procedure produced significantly greater accuracy, but both methods were imprecise and tended to produce high results.

It is evident that when no corrective measures for interfering materials are applied, the ECR procedure generally produces more accurate results than does aluminon. The precision obtained with either method, however, is poor. Nevertheless, the greater simplicity and speed of the ECR procedure make it preferable to aluminon.

The copper results indicate that all of the methods used are satisfactory at a level of 1.0 mg per liter, the threshold limit for drinking water. Unless it is established that bathocuproine or its disulfonate will give greater accuracy for a particular type of sample, the much higher cost of these chemicals ($17 to $25 per gram vs. 44¢ per gram for cuprethol) does not seem justified.

The Public Health Service Drinking Water Standards specify a threshold limit of 0.05 mg/l for manganese. This value is also stated to be the minimum detectable concentration for the standard persulfate and periodate methods. The formaldoxime method is claimed to be five times more sensitive. The results of this study indicate that both the persulfate and atomic absorption methods can measure this concentration with excellent accuracy but unacceptable precision, and there is insufficient data to draw any conclusions about the periodate method. A previous study has indicated, however, that the atomic absorption method is satisfactory if a Boling burner is used. The formaldoxime procedure, regardless of technique used to overcome iron interference, appears totally unacceptable. Some of the difficulty may be due to lack of clarity in the writeup of the procedure. It is not clear whether cyanide should be used even though iron is added to the standards. The amount of lead in the acetic acid solution used for precipitation of phosphates is not specified, and the interference level of phosphate is not stated.

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C. Manganese

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APPENDICES

APPENDIX A.

ALUMINUM RESULTS

Table A-1. Sample 1: Aluminum (0.48 mg/liter with fluoride)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2	0.000	1	3222	0.270	11
4	0.330	6	3226	0.450	6
4	0.720	12	3226	0.400	7
1114	0.434	10	3416	0.071	3
1114	0.515	3	3426	0.240	7
1124	0.530	8	3426	0.240	3
1124	0.410	4	3636	0.710	5
1124	0.540	1	3731	0.490	6
1124	0.500	14	3731	0.430	12
1222	0.740	4	4112	0.580	11
1314	0.500	1	4112	0.800	5
2223	0.300	6	4314	0.510	6
2223	0.470	16	4314	0.450	8
2411	0.485	11	4511	0.471	11
2411	0.445	5	4511	0.524	5
2526	1.300	10	4611	0.566	10
2611	0.580	10	4611	0.458	5
2611	0.470	2	4711	0.315	6
2626	0.479	5	4711	0.260	7
2626	0.520	10	4811	0.880	8
2926	0.960	3	4811	1.081	3
2926	0.000	10	4911	0.440	10
3221	0.490	6	4911	0.550	3
3221	0.500	13	5614	1.250	7

(Table A-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5614	0.460	1	7526	0.378	4
5622	0.270	6	7622	0.850	10
5626	0.480	1	7622	0.500	6
5626	0.250	7	7622	0.480	5
5811	0.370	7	7914	0.400	11
5811	0.510	6	8112	0.090	7
6112	0.050	7	8112	0.570	17
6112	0.750	6	8222	0.510	10
6311	0.530	5	8222	0.480	6
6314	0.920	6	8326	0.495	6
6314	0.660	7	9111	0.490	11
6622	0.280	7	9111	0.450	5
6622	0.660	5	9526	0.500	6
6715	0.580	6	9526	0.550	5
6816	1.840	7	9526	0.530	7
6816	0.032	4	9613	0.360	3
7112	0.320	10	9613	0.300	9
7112	0.340	5	9713	0.470	15
7216	0.480	5	9714	0.535	6
7216	0.410	11	9714	0.499	5
7222	0.440	5	9714	0.526	10
7222	0.440	7	9811	0.376	5
7522	0.522	5	9811	0.346	8
7526	0.264	10			

Table A-2. Sample 2: Aluminum (0.54 mg/liter with polyphosphate)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2	0.150	1	3226	0.360	1
4	0.200	2	3416	0.066	3
4	0.760	12	3426	0.200	3
1114	0.526	10	3426	0.300	7
1114	0.300	3	3636	0.320	5
1124	0.600	8	3731	0.480	6
1124	0.460	1	3731	0.440	12
1124	0.440	4	4112	0.800	1
1124	0.580	14	4112	1.000	7
1222	0.500	4	4314	0.490	8
1314	0.480	1	4314	0.460	2
2223	0.250	6	4511	0.584	2
2223	0.500	16	4511	0.476	8
2411	0.460	8	4611	0.398	2
2411	0.515	2	4611	0.318	8
2526	0.850	10	4711	0.400	7
2611	0.630	2	4711	0.280	1
2611	0.530	10	4811	1.040	8
2926	0.510	8	4811	1.033	3
2926	0.736	2	4911	0.480	10
3221	0.370	6	4911	0.400	3
3221	0.400	13	5614	0.380	1
3222	0.375	11	5614	0.500	7
3226	0.400	7	5622	0.208	2

(Table A-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5626	0.470	1	7526	0.388	10
5626	0.270	7	7622	0.420	7
5811	0.660	2	7622	0.520	1
5811	0.580	7	7914	0.520	8
6112	0.630	2	8112	0.160	7
6112	0.190	7	8112	0.540	17
6311	0.450	2	8222	0.450	4
6314	1.050	1	8222	0.500	10
6314	0.980	7	8326	0.525	2
6622	0.450	7	9111	0.476	2
6622	1.000	2	9111	0.500	8
6715	0.626	1	9526	0.610	7
6816	2.360	7	9526	0.600	5
6816	0.006	4	9526	0.640	6
7112	0.380	5	9613	0.200	4
7112	0.340	10	9613	0.330	9
7216	0.460	7	9713	0.500	15
7216	0.330	1	9714	0.501	5
7222	0.580	7	9714	0.559	7
7222	2.170	5	9714	0.495	6
7522	0.910	2	9811	0.108	8
7526	0.442	4	9811	0.148	2

Table A-3. Sample 3: Aluminum (0.52 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2	0.020	1	3226	0.490	1
4	0.500	1	3416	0.117	3
4	0.800	12	3426	0.440	7
1114	0.518	10	3426	0.230	3
1114	0.383	2	3636	0.810	5
1124	0.550	8	3731	0.700	6
1124	0.610	1	3731	0.600	12
1124	0.510	4	4112	1.100	2
1124	0.520	14	411	0.960	7
1222	0.940	4	4314	0.560	1
1314	0.440	1	4314	0.280	8
2223	0.460	6	4511	0.542	1
2223	0.490	16	4511	0.468	7
2411	0.485	7	4611	0.354	7
2411	0.485	1	4611	0.438	1
2526	0.200	10	4711	0.320	1
2611	0.560	2	4711	0.430	7
2611	0.480	10	4811	0.970	8
2926	0.688	1	4811	0.766	3
2926	0.400	7	4911	0.375	3
3221	0.500	1	4911	0.440	10
3221	0.510	13	5614	0.490	1
3222	0.400	11	5614	0.600	7
3226	0.500	7	5622	0.243	1

(Table A-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5626	0.500	1	7526	0.322	10
5626	0.500	7	7622	0.480	1
5811	0.460	7	7622	0.520	7
5811	0.550	1	7914	0.550	7
6112	0.830	1	8112	0.240	7
6112	0.210	7	8112	0.540	17
6311	0.420	1	8222	0.490	7
6314	0.860	1	8222	0.500	1
6314	0.840	7	8326	0.501	1
6622	0.480	7	9111	1.400	7
6622	0.805	1	9111	1.390	1
6715	0.650	1	9526	0.700	6
6816	2.360	7	9526	0.720	5
6816	0.014	4	9526	0.610	7
7112	0.490	10	9613	0.420	9
7112	0.500	5	9613	0.200	3
7216	0.410	1	9713	0.490	15
7216	0.410	7	9714	0.382	7
7222	0.666	7	9714	0.520	6
7222	0.850	5	9714	0.473	5
7522	0.635	1	9811	0.332	1
7526	0.396	4	9811	0.300	7

Table A-4. Sample 4: Aluminum (0.50 mg/liter with other metals)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2	0.070	1	3222	0.542	11
4	0.750	1	3226	0.750	1
4	1.520	12	3226	0.600	7
1114	0.545	10	3416	0.095	3
1114	0.485	3	3426	0.460	7
1124	0.640	8	3426	0.240	3
1124	0.670	1	3636	0.680	5
1124	0.690	4	3731	0.620	6
1124	0.530	14	3731	1.220	12
1222	0.450	4	4112	0.580	1
1314	0.590	1	4112	0.760	7
2223	0.450	6	4314	0.790	8
2223	0.520	16	4314	0.706	1
2411	0.620	7	4511	0.505	1
2411	0.620	1	4511	0.579	7
2526	0.900	10	4611	0.461	7
2611	0.670	2	4611	0.561	1
2611	0.620	10	4711	0.560	7
2626	0.497	1	4711	0.284	1
2626	0.518	7	4811	0.980	8
2926	0.560	1	4811	1.051	3
2926	0.550	7	4911	0.480	10
3221	0.480	1	4911	0.425	3
3221	0.710	13	5614	1.300	7

(Table A-4 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5614	0.600	1	7622	0.640	7
5622	0.293	1	7622	0.520	1
5811	0.600	7	7914	0.660	7
5811	0.550	1	8112	0.400	7
6112	1.400	1	8112	0.600	17
6112	0.380	7	8222	0.500	7
6311	0.430	2	8222	0.450	1
6314	1.100	1	8326	0.500	1
6314	1.080	7	9111	0.587	7
6622	0.630	1	9111	0.583	1
6622	0.700	7	9526	0.650	7
6715	0.675	1	9526	0.680	6
6816	1.880	7	9526	0.690	5
6816	0.011	4	9613	0.520	9
7112	0.570	5	9613	0.240	3
7112	0.600	10	9713	0.520	15
7216	0.430	1	9714	0.560	6
7216	0.430	7	9714	0.460	7
7222	0.860	7	9714	0.495	5
7222	0.970	5	9811	0.420	1
7522	0.575	1	9811	0.468	7
7526	0.438	10			

APPENDIX B.

COPPER RESULTS

Table B-5. Sample 4: Copper (1.00 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4	1.010	1	4112	1.000	1
1114	1.000	1	4524	0.940	1
1124	1.000	2	4611	0.960	1
1124	1.000	4	4711	1.000	2
1222	0.980	1	4711	1.040	1
2223	0.940	1	4911	0.980	1
2223	1.000	4	5622	0.950	2
2411	1.000	1	5622	0.980	1
2411	1.050	4	5626	1.000	2
2526	0.210	1	5626	1.000	1
2526	0.765	2	6112	1.000	2
2611	1.100	1	6112	0.970	1
2626	1.010	4	6113	1.220	1
2926	1.000	1	6311	1.060	1
3221	1.000	1	6314	0.850	6
3222	1.021	2	6622	0.920	1
3226	1.050	1	6622	0.970	2
3226	1.050	4	6715	0.990	1
3416	0.770	4	6816	0.710	1
3426	0.940	2	7112	1.030	1
3636	1.050	1	7112	1.020	4
3731	1.100	1	7216	0.980	2
3731	1.140	3	7216	0.990	1
3731	1.020	5	7216	1.000	4

(Table B-5 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7222	1.020	1	9111	1.000	1
7222	1.000	2	9111	1.004	2
7522	1.037	2	9526	0.960	2
7522	1.028	1	9526	0.980	1
7526	0.980	1	9613	1.000	4
7622	0.980	1	9613	1.000	1
7914	1.000	2	9713	1.500	4
8112	1.000	4	9714	1.000	4
8222	0.950	2	9714	1.010	2
8222	1.060	1	9811	1.000	2
8326	0.970	1			

APPENDIX C.
MANGANESE RESULTS

Table C-6. Sample 4: Manganese (0.05 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2	0.010	5	3226	0.070	2
4	0.120	2	3416	0.027	2
1114	0.048	2	3416	0.028	9
1124	0.050	1	3426	0.100	4
1124	0.050	7	3636	0.074	2
1124	0.050	9	3731	0.350	7
1222	0.045	1	3731	0.270	1
1222	0.000	7	4112	0.300	6
2223	0.040	9	4524	0.100	1
2223	0.040	2	4611	0.047	3
2411	0.100	3	4711	0.050	8
2411	0.050	8	4711	0.050	9
2411	0.050	9	4711	0.000	3
2526	0.150	1	4911	0.264	2
2526	0.100	7	5622	0.070	7
2611	0.045	9	5626	0.125	2
2611	0.050	7	5811	0.090	2
2611	0.150	3	6112	0.100	2
2626	0.052	9	6112	0.050	7
2926	0.188	6	6113	0.320	3
3221	0.100	2	6311	0.080	3
3222	0.011	1	6311	0.054	7
3222	0.008	8	6622	0.125	3
3226	0.050	9	6622	0.055	8

(Table C-6 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6715	0.049	7	8222	0.040	7
6715	0.200	3	8222	0.300	3
6816	0.105	1	8326	0.090	1
7112	0.030	9	9111	0.050	7
7214	0.070	7	9111	0.050	1
7216	0.070	9	9526	0.200	2
7222	0.250	7	9526	0.090	3
7522	0.080	7	9526	0.100	7
7522	0.060	2	9613	0.270	1
7526	0.060	1	9714	0.048	8
7622	0.046	7	9714	0.050	9
7622	0.044	3	9714	0.052	7
7914	0.000	3	9714	0.051	3
7914	0.000	7	9811	0.050	7
8112	0.046	9			

APPENDIX D.

ERIOCHROME CYANINE R METHOD FOR ALUMINUM

Aluminum is the third most abundant element of the earth's crust, occurring in minerals, rocks, and clays. This wide distribution accounts for the presence of aluminum in practically all natural water supplies, as a soluble salt, colloid, or insoluble compound. Soluble, colloidal, and insoluble aluminum may appear additionally in treated water as a residual from alum coagulation. There are many conflicting statements in the literature about the amount of this residual, but recent work[1] indicates that filtered water from a modern rapid sand filtration plant should have an aluminum concentration between 0.02 and 0.05 mg/l.

1. General Discussion

1.1. Principle: Dilute aluminum solutions buffered to a pH of 6.0 produce with Eriochrome Cyanine R dye a red to pink complex that exhibits maximum absorption at 535 mμ. The intensity of the developed color is influenced by the aluminum concentration, reaction time, temperature, pH, alkalinity, and the concentration of other accompanying ions in the sample. To compensate for color and turbidity, the aluminum in one portion of sample is complexed with EDTA to provide a blank. The interference of iron and manganese, two elements that are often found in water, are eliminated by the addition of ascorbic acid. The optimum aluminum range lies between 0.02 and 0.35 mg/l but can be extended upward by sample dilution.

1.2. Interference: Negative errors are caused by both fluorides and polyphosphates. When the fluoride concentration is constant, the percentage of error decreases with increasing amounts of aluminum. As the fluoride concentration is often known, or can readily be determined, fairly accurate results can be obtained by adding the known amount of fluoride to a set of standards. If less accuracy can be tolerated, a simpler correction can be determined from the family of curves in Figure 1. A procedure is given for the removal of complex phosphate interference. Orthophosphates in concentrations under 10 mg/l do not interfere. The interference caused by even small amounts of alkalinity is removed by acidifying the sample just beyond the neutralization point of methyl orange. Sulfates do not interfere up to a concentration of 2000 mg/l.

1.3. Minimum detectable concentration: The minimum aluminum concentration detectable by this method in the absence of fluorides and complex phosphates is approximately 6 μg/l.

1.4. Sample handling: Samples should be collected in clean, acid-rinsed bottles and should be examined as soon as possible after collection. If the concentration of soluble aluminum only is desired, a portion of the sample should be filtered through a 0.45 μ membrane filter and the filtrate used for the determination. Filter paper, absorbent cotton, and glass wool are completely unsuited for filtering any solution that is to be tested for aluminum, as they will remove most of the soluble aluminum.

2. Apparatus

2.1. Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at 535 mμ and utilizing a light path of 1 cm or longer.

b. Filter photometer, providing a light path of 1 cm or longer and equipped with a green filter showing maximum transmittance between 525-535 mμ.

c. Nessler tubes, 50 ml, tall form, matched.

2.2. Glassware: All glassware must be treated with warm 1 + 1 HCl and then rinsed with aluminum-free distilled water to avoid errors due to materials adsorbed on the glass. Rinse sufficiently to remove all acid.

3. Reagents

Use reagents low in aluminum and aluminum-free distilled water.

3.1. Stock aluminum solution: The metal (a) or the salt (b) may be used for the preparation of the stock solution, which contains 0.500 mg Al per 1.00 ml:

a. Dissolve 0.5000 g ACS grade aluminum metal in 10 ml of conc. HCl by heating gently. Dilute to 1 liter in a volumetric flask with distilled water.

b. Dissolve 8.792 g potassium aluminum sulfate (also called potassium alum), $K_2Al_2(SO_4)_4 \cdot 24\,H_2O$, in distilled water and dilute to 1 liter in a volumetric flask.

3.2. Standard aluminum solution: Dilute 10.00 ml of the stock aluminum solution to 1 liter in a volumetric flask with distilled water; 1.00 ml = 5 μg Al. Prepare daily.

3.3. Sulfuric acid: 0.02 N and 6 N.

3.4. Ascorbic acid solution: Dissolve 0.1 g ascorbic acid in distilled water and make up to 100 ml in a volumetric flask. Prepare fresh daily.

3.5. Buffer solution: Dissolve 136 g sodium acetate, $CHCOONa \cdot 3H_2O$, in water, add 40 ml 1-N acetic acid, and dilute to 1 liter.

3.6. Stock dye solution: A number of products are available. Any of the following may be used.

a. Solochrome cyanine R-200[1] or eriochrome cyanine[2]: Dissolve 100 mg of the dye in distilled water, and dilute to 100 ml in a volumetric flask. This solution should have a pH value of about 2.9.

b. Eriochrome cyanine R[3]: Dissolve 300 mg of the dye in about 50 ml distilled water. Adjust the pH value, which will be about 9, to about 2.9 with 1 + 1 acetic acid. Approximately 3 ml will be required. Dilute with distilled water to 100 ml.

c. Eriochrome cyanine R[4]: Dissolve 150 mg of the dye in about 50 ml distilled water. Adjust the pH value, which will be about 9, to about 2.9 with 1 + 1 acetic acid. Approximately 2 ml will be required. Dilute with distilled water to 100 ml.

Stock solutions, prepared as described above, have excellent stability. They can be kept for at least a year, and perhaps longer.

3.7. Working dye solution: Dilute 10.0 ml of any one of the stock dye solutions to 100 ml in a volumetric flask with distilled water. Working solutions are stable for at least 6 months.

3.8. Methyl orange indicator solution.

3.9. 0.01 M EDTA (di-sodium ethylene-diamine tetra acetate): Weigh 3.7 g of the reagent, dissolve in distilled water, and dilute to 1 liter.

3.10. Sodium hydroxide, 1 N and 0.1 N.

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[1] A product of Arnold Hoffman and Co., Providence, R.I.

[2] A product of K & K Labs., Plainview, N.Y.

[3] A product of Pfaltz and Bauer, Inc., Flushing, N.Y.

[4] A product of Hartman-Leddon Co., Philadelphia.

4. Procedure

Preparation of Calibration Curve:

4.1. Prepare a series of aluminum standards from 0 to 7 μg (0 - 280 μg/l based on a 25 ml sample) by accurately measuring the calculated volumes of standard aluminum solution into 50 ml volumetric flasks or nessler tubes. Add distilled water to a total volume of approximately 25 ml.

4.2. Add 1 ml 0.02 N sulfuric acid to each standard and mix. Follow with 1 ml ascorbic acid solution and mix.

4.3. Add 10 ml buffer solution and mix.

4.4. Using a volumetric pipette, add 5 ml of working dye reagent and mix. Immediately make up to a volume of 50 ml with distilled water. Mix and let stand for 5 to 15 min. The color begins to fade after 15 min.

4.5. Read the transmittance or absorbance on a spectrophotometer using a wavelength of 535 mμ or a green filter providing maximum transmittance between 525 and 535 mμ. Adjust the instrument to 100 per cent transmittance or zero absorbance with the standard containing no aluminum.

4.6. Plot a calibration curve relating micrograms aluminum to the instrument reading.

Sample Treatment in the Absence of Fluoride and Complex Phosphates:

4.7. Place a 25.0 ml sample, or an aliquot diluted to 25 ml, in a porcelain dish or flask, add a few drops of methyl orange indicator, and titrate with 0.02 N sulfuric acid to a faint pink color. Record reading and discard this sample.

4.8. To two similar samples, at room temperature, add the same amount of 0.02 N acid used in the titration and 1 ml in excess.

4.9. To one of the samples add 1 ml EDTA solution. This one will serve as a blank by complexing any aluminum present and compensating for color and turbidity.

4.10. Add 1 ml ascorbic acid to the blank and sample, and continue to follow the procedure from 4.3 through 4.4.

4.11. Set the instrument to zero absorbance or 100 percent transmittance using the EDTA blank. Read the transmittance or absorbance

of the sample and determine the aluminum concentration from the previously prepared calibration curve.

4.12. If photometric equipment is not available, prepare and treat the standards and a sample, as described above, in 50 ml nessler tubes. Make up to the mark with distilled water, and compare the color of the sample with the standards after a 5 to 15 min. contact time. A sample treated with EDTA is not needed when nessler tubes are used. If the sample contains turbidity or color, the use of nessler tubes may result in considerable error.

Removal of Phosphate Interference:

4.13. Add 1.7 ml 6 N sulfuric acid to 100 ml of sample in a 200 ml Erlenmeyer flask.

4.14. Heat on a hot plate for at least 90 minutes, keeping the solution temperature just below the boiling point.

4.15. At the end of the heating period, the solution volume should be about 25 ml. Add distilled water whenever necessary to keep it at or above that volume.

4.16. After cooling, using a pH meter, neutralize the solution to a pH value between 4.3 and 4.5 with sodium hydroxide, using 1 N hydroxide at the start and 0.1 N for the final fine adjustment.

4.17. Make up to 100 ml with distilled water, mix, and use a 25 ml aliquot for the aluminum test.

4.18. Run a blank in the same manner using 100 ml of distilled water and 1.7 ml 6 N sulfuric acid; subtract it from the sample, or use it to set the instrument to zero absorbance or 100 percent transmittance before reading the sample.

Sample Treatment in the Presence of Fluoride:

4.19. Measure the fluoride concentration of the sample by the SPADNS method or electrode method, using sufficient citrate solution to complex the aluminum.

4.20. Perform one of the following:

a. Add the same amount of fluoride as in the sample to each aluminum standard.

b. Determine the fluoride correction from the set of curves in Figure 1. This method may be used when a slight loss in accuracy can be tolerated.

5. Calculation

$$\text{mg/l Al} = \frac{\mu\text{g Al}}{\text{ml sample}}$$

Bibliography

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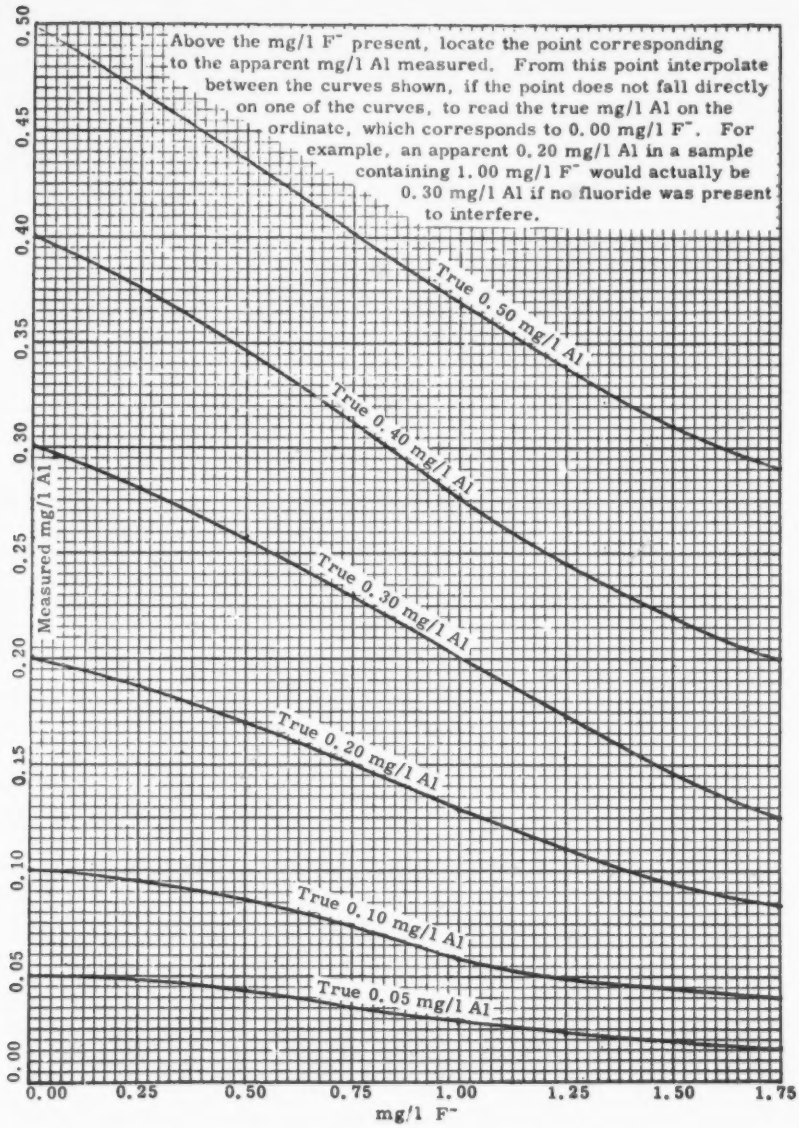
Above the mg/l F⁻ present, locate the point corresponding to the apparent mg/l Al measured. From this point interpolate between the curves shown, if the point does not fall directly on one of the curves, to read the true mg/l Al on the ordinate, which corresponds to 0.00 mg/l F⁻. For example, an apparent 0.20 mg/l Al in a sample containing 1.00 mg/l F⁻ would actually be 0.30 mg/l Al if no fluoride was present to interfere.
True 0.50 mg/l Al
True 0.40 mg/l Al
True 0.30 mg/l Al
True 0.20 mg/l Al
True 0.10 mg/l Al
True 0.05 mg/l Al
Measured mg/l Al
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
mg/l F⁻

Figure 1. True mg/l aluminum curves.

APPENDIX E.

BATHOCUPROINE DISULFONATE METHOD FOR COPPER

1. General Discussion

1.1. Principle: Cuprous ions form a water soluble orange-colored chelate with bathocuproine disulfonate. Despite the fact that the color forms over the pH range of 3.5 to 11.0, the recommended pH range is between 4 and 5. Hydrochloric acid and citrate buffer the system at a pH of about 4.3, and hydroxylamine hydrochloride serves as a reducing agent. The absorbance is measured at 484 mμ. The method can be applied to copper concentrations up to at least 5 mg/l with a sensitivity of 0.02 mg/l.

1.2. Interference: The following ions and substances can be tolerated with an error of less than ±2 percent.

Ion	mg/l	Ion	mg/l
Aluminum	100	Thorium (IV)	100
Beryllium	10	Zinc	200
Cadmium	100	Chlorate	1000
Calcium	1000	Chloride	1000
Chromium (III)	10	Fluoride	500
Cobalt (II)	5	Nitrate	200
Iron (II)	100	Nitrite	200
Iron (III)	100	Orthophosphate	1000
Lithium	500	Perchlorate	1000
Magnesium	100	Sulfate	1000
Manganese (II)	500	Residual chlorine	1
Nickel (II)	500	Linear alkylate sulfonate (LAS)	40
Sodium	1000		
Strontium	200		

Cyanide, thiocyanate, persulfate, and EDTA also can interfere.

1.3. Minimum detectable concentration: 20 μg/l when a 5-cm cell is used in a spectrophotometer.

1.4. Absorptivity: 0.164 liter/mg cm.

2. Apparatus

2.1. Colorimetric equipment: One of the following, equipped with absorption cells and providing light paths of 1 to 5 cm (the latter is recommended), is required.

a. Spectrophotometer, for use at 484 mμ.

b. Filter photometer, equipped with a blue-green filter (similar to a Wratten No. 45) exhibiting maximum light transmission near 484 mμ.

c. Nessler tubes, matched, 100 ml, tall form.

2.2. Acid-washed glassware: All glassware must be rinsed with concentrated HCl and then with copper-free water.

3. Reagents

3.1. Copper-free water: The water used throughout this procedure must be prepared by either redistilling single-distilled water from an all-pyrex still or by passing distilled water through a mixed bed of ion-exchange resins [see General Introduction, Sec. 2, and Nitrogen (Ammonia), Method A, Sec. 3.1b, SMEWW, 12th Edition].

3.2. Stock copper solution: Weigh 100.0 mg 99.9 percent pure copper wire or foil; place in a 250-ml beaker under a hood; add 3 ml copper-free water and 3 ml concentrated nitric acid, and cover the beaker with a watch glass. After dissolving all of the metal, add 1 ml concentrated sulfuric acid and heat on a hot plate to volatilize the acids. Stop heating just short of complete dryness. Do not bake the residue. Cool and dissolve in copper-free water, washing down the sides of the beaker and bottom of the watch glass. Transfer quantitatively to a 1-liter volumetric flask, and make up to the mark with copper-free water. This stock solution contains 100 μg Cu per 1.00 ml.

3.3. Standard copper solution: Dilute 50.00 ml stock copper solution to 1000 ml with copper-free water; 1.00 ml = 5.0 μg Cu.

3.4. Hydrochloric acid, 1 + 1. Use copper-free water.

3.5. Hydroxylamine hydrochloride solution: Dissolve 100 g $NH_2OH \cdot HCl$ in 900 ml copper-free water.

3.6. Sodium citrate solution: Dissolve 300 g $Na_3C_6H_5O_7 \cdot 2H_2O$ in copper-free water and make up to 1 liter.

3.7. Disodium bathocuproine disulfonate solution: Dissolve 1.000 g $C_{12}H_4N_2(CH_3)_2(C_6H_4)_2(SO_3Na)_2$ in copper-free water and make up to the mark in a 1-liter volumetric flask.

4. Procedure

Pipet 50.0 ml sample, or a suitable aliquot diluted to 50.0 ml, into a 250-ml erlenmeyer flask. In separate 250-ml erlenmeyer flasks,

prepare a 50.0-ml redistilled water blank and a series of 50.0-ml copper standards containing 5.0, 10.0, 15.0, 20.0, and 25.0 μg Cu. To sample, blank, and standards add, mixing after each addition, 1.00 ml 1 + 1 HCl, 5.00 ml hydroxylamine hydrochloride solution, 5.00 ml sodium citrate solution, and 5.00 ml disodium bathocuproine disulfonate solution. Transfer to cells, and read the absorbance of the sample against the blank at 484 mμ. Plot absorbance against μg Cu in standards for the calibration curve. Estimate the copper concentration of the sample from the calibration curve.

5. Calculation

$$\text{mg/l Cu} = \frac{\mu\text{g Cu}}{\text{ml sample}}$$

6. Precision and Accuracy

When photometric measurements are made in 5-cm cells, the method is estimated to have a precision of ±0.02 mg/l Cu and an accuracy of ±6 percent in the neighborhood of 300 μg/l Cu.

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APPENDIX F.

FORMALDOXIME METHOD FOR MANGANESE

The colorimetric determination of manganese by means of the permanganate ion system is quite specific but not particularly sensitive. The tetrabase procedure is sensitive, but the color is not stable. The formaldoxime procedure is sensitive and stable but not entirely specific because iron, phosphates, and sucrose interfere. The manganese color develops more quickly than the iron color. Cyanide can sequester the iron, but the time for manganese color to fully develop is increased thereby.

1. General Discussion

1.1. Principle: The manganous complex reacts with formaldoxime to form a trivalent manganese formaldoxime colored compound that gives a straight line photometric plot with increasing manganese concentration. The color develops at 10 μg/l in a 10-ml sample, while 50 μg/l manganese (or 5 μg per 100-ml sample) are required in the permanganate ion color method.

1.2. Interference: Soluble iron interferes with the manganese, although the iron color develops much more slowly than the manganese. Use of cyanide ties the iron present, but, if the sample contains iron, this should be determined by the phenanthroline method (see page 154, 12th Edition of Standard Methods for the Examination of Water and Wastewater) and for accurate manganese determination approximately the same amount of iron must be added to the standards from a stock solution containing 100 μg ferric ion per ml. Iron interference can be avoided by warming the solution for 2 hours at 65°C after adding formaldoxime reagent. The color due to iron will be removed at the end of 2 hours. Also, a high concentration of phosphates present in the sample will interfere with the determination by reducing the color. The interference of phosphates, however, can be eliminated by the precipitation of the phosphates with lead in an acetic acid solution. Calcium and magnesium form a precipitate in the alkaline solution and must be removed from the solution by filtration before developing the color. The presence of more than 50 micromoles sucrose (16 mg/l) in the sample will interfere, but the interference in color development is linear with respect to manganese concentration. Therefore, the addition of sucrose to the standards will take care of this interference, except that the color is not stable and readings must be taken within 2 hours. The color in the presence of sucrose fades completely in 24 hours.

1.3. Minimum detectable concentration: 10 μg/l Mn.

2. Apparatus

2.1. Colorimetric equipment: One of the following is required.

a. Spectrophotometer, for use at 450 mμ and providing a light path of 2.5 cm (1 inch) or 1 cm.

b. Filter photometer, providing a light path of 2.5 cm or 1 cm and equipped with violet color filter having a maximum transmittance near 450 mμ.

2.2. Test tubes: 1 cm or 2.5 cm (1 inch) diameter.

3. Reagents

3.1. Potassium hydroxide solution: Dissolve 40 g KOH in 100 ml carbon dioxide-free distilled water.

3.2. Peptone solution: Dissolve 5 g peptone in distilled water and dilute to 100 ml. Prepare daily.

3.3. Formaldoxime reagent: Dissolve 20 g paraformaldehyde,* also called trioxymethylene, and 47 g hydroxylamine sulfate by boiling in 100 ml distilled water.

3.4. Standard manganese solution: Dissolve 406 mg manganese sulfate tetrahydrate, $MnSO_4 \cdot 4H_2O$, in distilled water containing 1.0 ml concentrated sulfuric acid, and dilute to 1000 ml; 1.00 ml = 100 μg Mn. Prepare manganese standards of lower concentration by dilution with distilled water.

3.5. Special reagents required for iron interference:

a. Sodium cyanide solution: Dissolve 20 g NaCN in 100 ml distilled water. (CAUTION: Sodium cyanide is extremely poisonous and more than customary precautions should be observed in its handling. Never use mouth pipets to deliver volumes of cyanide solution. Instead, rely on an automatic, dropping, or safety pipet; and avoid inhalation or exposure to the skin.)

b. Ferric chloride solution: Dissolve 400 mg $FeCl_3 \cdot 6H_2O$ in 1 liter distilled water, and add 5 ml of 0.077N hydrochloric

* Available from Allied Chemical Co., General Chemical Division, New York, N.Y., as catalog no. 2045; or from Distillation Products Industries, Eastman Organic Chemicals Dept., Rochester, N.Y. 14603, as catalog no. 421.

acid to form a solution containing 100 μg ferric ion per ml. Add this solution to the manganese standards with a microburet.

4. Procedure

4.1. Absence of iron in sample: Add 5 drops (0.25 ml) potassium hydroxide solution to 10 ml sample and mix. Add 1 drop (0.05 ml) peptone solution, mix thoroughly, add 3 drops (0.15 ml) formaldoxime reagent, and agitate; a wine red color develops immediately. Wait about 20 minutes for full color development, then measure the absorbance at 450 mμ.

4.2. Presence of iron in sample: Add 10 drops (0.5 ml) sodium cyanide solution after adding the potassium hydroxide solution. Then follow the procedure described in Section 4.1.

4.3. Preparation of standard curve: Treat manganese standards in the range of 0 to 3.0 mg/l (0 to 30 mg Mn) in the same manner as the sam[illegible]

5. Calculation

$$\text{mg/l Mn} = \frac{\mu\text{g Mn}}{\text{ml sample}}$$

6. Precision and Accuracy

In the presence of iron, the error may be as large as 15 percent, but this can be avoided by careful modifications in the manganese calibration standards.

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APPENDIX G.
GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms defined as they are used in this report is presented to ensure uniformity of understanding.

Arithmetic mean — The sum of the sample results divided by the number of results in the sample. Let X_i ($i = 1, 2, \ldots, n$) denote the i^{th} results in a sample of n results. The arithmetic mean denoted $\overline{X}$ is given by $\overline{X} = \sum_{i=1}^{n} \frac{X_i}{n}$.

Median — Halfway point in the results when they have been arranged in order of magnitude (the middle result of an odd number of results, or the average of the middle two for an even number).

Accuracy — The correctness of a measurement, or the degree of correspondence between the results and the true value (actual amount added).

Measures of accuracy — Measures that relate to the difference between the mean of the results and the true value when the latter is known or assumed. The following measures apply:

Mean error – The average difference with regard to sign between the results and the true value. Equivalently, the difference between the mean of the results and the true value (T. V.).

$$\text{Mean error} = \overline{X} - \text{T. V.}$$

Relative error – The absolute value of the mean error expressed as a percentage of the true value.

$$\text{Relative error} = \frac{|\overline{X} - \text{T. V.}|}{\text{T. V.}} \times 100$$

Precision — The reproducibility of sample results or the degree of agreement among the results.

Measures of precision

Measures of the variation among the sample results themselves, i.e., the spread or dispersion of the results without regard to the true value. The following measures apply.

Sample variance – Sum of squared deviations of the sample results from their mean divided by one less than the number of results in the sample. The sample variance denoted s^2 is given by

$$s^2 = \frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}$$

where n is the number of results.

Sample standard deviation – Square root of the sample variance.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}}$$

Relative standard deviation (coefficient of variation) – Sample standard deviation expressed as a percentage of the mean.

$$\text{Rel. Std. Dev.} = \frac{s}{\bar{X}} \times 100$$

Range – The difference between the largest and smallest results in the sample.

Confidence limits – Limits within which the true mean, μ, of the population (the theoretically infinite number of possible replications of the analysis) will lie with probability equal to $1 - \alpha$, where α is the probability that the limits do not contain the true mean. The upper and lower $1 - \alpha$ confidence limits are given by

$$\text{Confidence limits} = \bar{X} \pm t_{\alpha/2} s/\sqrt{n}$$

where $\overline{X}$ and s are the sample mean and standard deviation, $t_{\alpha/2}$ is the upper $\alpha/2$ point of "Student's" t-distribution, and n is the number of results in the sample used to compute $\overline{X}$.

Tolerance limits – Limits within which one can state with probability γ that at least a proportion P of the entire population will lie. The upper and lower tolerance limits are given by,

$$\text{Tolerance limits} = \overline{X} \pm Ks,$$

where $K^{(1)}$ is the factor for two-sided tolerance limits for normal populations. The value of K depends upon the chosen values of γ and P.

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APPENDIX H.

TESTS FOR NORMALITY AND REJECTION OF OUTLIERS

Test for normality

The Kolmogorov-Smirnov goodness-of-fit test was used to determine whether the observations reported could reasonably be thought to have come from a normal distribution.[1]

Briefly, the test involves computing the observed cumulative frequency distribution (the percent of values less than or equal to each value in the distribution) and comparing it with the theoretical normal cumulative frequency distribution. The point at which the two distributions, theoretical and observed, show greatest divergence is determined. Reference of the value of the divergence to a table of critical values for the Kolmogorov-Smirnov goodness-of-fit test indicates whether such a large divergence is likely on the basis of chance. If such a large divergence is not likely, the distribution is designated as nonnormal; otherwise the distribution is designated as normal.

Tests for rejection of outliers

1. If the distribution is designated as nonnormal, the suspected outlier (the farthest value from the mean) is rejected only if the distance between it and the mean is greater than three standard deviations; otherwise the suspected outlier is accepted.

2. If the distribution is designated as normal and the sample size is less than or equal to 30, the suspected outlier, the farthest value from the mean, is tested for rejection by a method developed by Dixon.[2] Briefly, this test involves computing a ratio that compares the distance of the suspected value being tested from its neighbors with the range of all, or most all, of the observations (depending on the total number of suspected values in the sample). Reference of the ratio to a table of critical values for test ratios for gross errors indicates whether such a large ratio is likely on the basis of chance. If the ratio is greater than or equal to the critical value, the probability that the suspected outlier is from the sample distribution is small; hence, the outlier is rejected. If the ratio is less than the critical value, the suspected outlier probably came from the sample distribution; hence, the suspected outlier is accepted.

3. If the distribution is designated as normal, and the sample size is greater than 30, the suspected outlier is tested for rejection by a method developed by Santner.[3] This method employs the statistic, $\frac{\overline{X} - X_o}{s}$, where $\overline{X}$ is the sample mean, X_o is the suspected outlier (the

farthest value from the mean), and s is the sample standard deviation. This statistic is compared to a table of critical values to determine whether its value is larger than would be expected on the basis of chance. If the statistic is greater than or equal to the critical value, the suspected outlier is rejected; otherwise, the suspected outlier is accepted.

Application of tests for normality and for rejection of outliers to ARS studies

The test for normality and the subsequent test for rejection of outliers are applied to the observed data in two ways: first, to each method for a given substance at a given level of concentration; then to a given substance at a given level of concentration regardless of method. In either case, it is first necessary to determine whether the original distribution is normal or nonnormal. If the original distribution is designated as nonnormal, method 1 is used to test for rejection of the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests for normality or rejection of outliers are made, and the distribution is designated as nonnormal. On the other hand, if the suspected outlier is rejected, the new distribution, which excludes the rejected observation, is then tested for normality. If the new distribution is nonnormal, the next suspected outlier is tested for rejection by method 1. This cycle of testing for normality and testing for rejection of outliers continues until a suspected value is not rejected or the test for normality designates the distribution as normal. If the distribution is designated as normal, subsequent tests for rejection of outliers made by method 2 or 3 are the same as if the original distribution had been normal. This case is discussed next.

If the original distribution is designated as normal or a new distribution that was originally nonnormal is designated as normal after the rejection of one or more outliers, and if the number of observations is not greater than 30, then method 2 is used to test for rejection the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution is tested for rejection, and so on until the suspected value of a new distribution is not rejected; when this occurs, no further tests are made, and the final distribution is designated as normal. On the other hand, if the number of observations in the original distribution is greater than 30, method 3 is used to test the suspected outlier for rejection. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution, which excludes the rejected value, is tested for rejection. Testing for outliers continues by this method until a suspected outlier is not rejected or the number of

observations is no longer greater than 30; in which case, method 2 is used for testing for rejection of any remaining suspected outliers.

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APPENDIX I.

COMPARISON OF METHODS FOR STATISTICALLY SIGNIFICANT DIFFERENCES IN PRECISION AND ACCURACY

The methods are compared in two ways with respect to precision and accuracy. In the first case, two methods are compared at a given level of concentration with respect to precision and to accuracy. The unknown variances, σ_1^2 and σ_2^2 (estimated by the sample variances, s_1^2 and s_2^2), of the two methods are first compared by the F-test[1] to determine whether there is a significant difference in the precision of the two methods. The unknown means, μ_1 and μ_2 (estimated by the sample means, $\overline{X}_1$ and $\overline{X}_2$), of the two methods then are compared by the t-test[2] to determine whether there is a significant difference in the accuracy of the two methods. The t-test employed is based on the result of the F-test. These two tests of hypotheses will produce one of the following results.

Outcome 1: $\sigma_1^2 = \sigma_2^2$, $\mu_1 = \mu_2$

Outcome 2: $\sigma_1^2 = \sigma_2^2$, $\mu_1 \neq \mu_2$

Outcome 3: $\sigma_1^2 \neq \sigma_2^2$, $\mu_1 = \mu_2$

Outcome 4: $\sigma_1^2 \neq \sigma_2^2$, $\mu_1 \neq \mu_2$

In outcome 1, we conclude that the sample results do not indicate that a significant difference in either precision or accuracy exists between the two methods.

In outcome 2, we conclude that there is no indication of a significant difference in precision between the two methods, but there is a significant difference in the accuracy of the two methods; specifically, the method whose sample mean is closer to the true value is deemed the more accurate. In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the two methods, but the method with the smaller sample variance is the more precise.

In outcome 4, we conclude that there is a significant difference in the precision and in the accuracy of the two methods. The method with the smaller sample variance is the more precise, and the method whose sample mean is closer to the true value is the more accurate.

In the second case, more than two methods are compared at a given level of concentration with respect to precision and accuracy. Bartlett's Test[3] is used first to test the hypothesis of equality of the unknown variances, σ_i^2, of the methods in order to compare the precision of the methods. If we conclude that the precision is the same, the Analysis of Variance[4] is then used to test whether a significant difference exists among the means, μ_i, in order to compare the accuracy of the methods. If there is a significant difference among the means. Duncan's Multiple Range Test[5, 6] is used to determine which method means differ significantly. If the precision is not the same, then the Kruskal-Wallis One-way Analysis of Variance by Ranks[7] is used to determine whether a significant difference exists among the means in order to compare the accuracy of the methods.

Once again, there are basically four possible outcomes for the above tests of hypotheses.

Outcome 1: all σ_i^2 are equal, all μ_i are equal

Outcome 2: all σ_i^2 are equal, not all μ_i are equal

Outcome 3: not all σ_i^2 are equal, all μ_i are equal

Outcome 4: not all σ_i^2 are equal, not all μ_i re equal

In outcome 1, we conclude that the sample results do not indicate a significant difference in either the precision or the accuracy of the methods.

In outcome 2, we conclude that there is no indication of a significant difference in the precision of the methods; however, at least one method does differ significantly from the rest with respect to accuracy, and Duncan's Multiple Range Test indicates which methods differ. For example, in comparing four methods, we might conclude $\mu_1 = \mu_2$ and $\mu_3 = \mu_4$, but μ_1 and μ_2 differ significantly from μ_3 and μ_4; or we might conclude that $\mu_1 = \mu_2 = \mu_3$, but μ_4 differs significantly from μ_1, μ_2, and μ_3.

In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the methods, but at least one method differs significantly from the rest with respect to precision.

In outcome 4, we conclude that the methods differ significantly with respect to both precision and accuracy.

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APPENDIX J.

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